

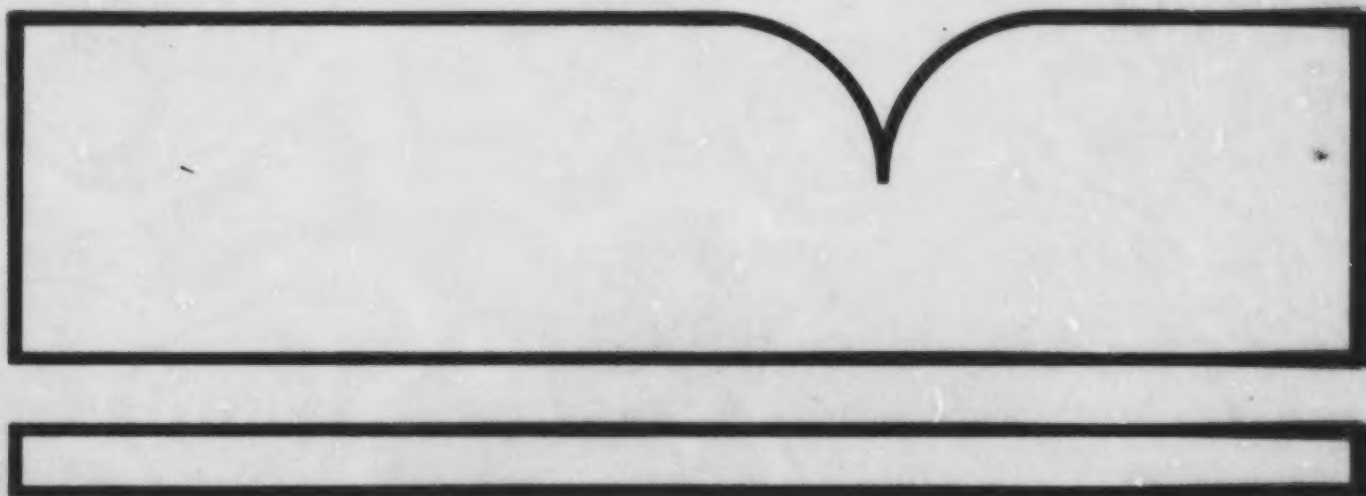
Halogenated Organics Study for Allen
Kingston, and Shawnee Steam Plants

(U.S.) Tennessee Valley Authority
Chattanooga

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

May 81



U.S. Department of Commerce
National Technical Information Service

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EPA-600/7-81-094
May 1981

Tennessee Valley
Authority
Office of Power

Energy Demonstrations
and Technology
Chattanooga TN 37401

TVA/OP/EDT-81/25

Halogenated Organics Study for Allen, Kingston, and Shawnee Steam Plants

Interagency
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R&D Program Report



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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/7-81-094		2.		3. RECIPIENT'S ACCESSION NO. PR67 119225	
4. TITLE AND SUBTITLE Halogenated Organics Study for Allen, Kingston, and Shawnee Steam Plants				5. REPORT DATE May 1981	
7. AUTHOR(S) C. V. Seaman, H. B. Flora II, L. O. Hill (TVA); B. W. Vigon, T. B. Stanford, M. D. Hunter (Battelle)				6. PERFORMING ORGANIZATION CODE U289030	
9. PERFORMING ORGANIZATION NAME AND ADDRESS TVA 1140 Chestnut Street, Tower II Chattanooga, Tennessee 37401				8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711				10. PROGRAM ELEMENT NO. INE624A	
				11. CONTRACT/GRANT NO. IAG-D5-E721	
15. SUPPLEMENTARY NOTES IERL-RTP project officer is Julian W. Jones, Mail Drop 61, 919/541-2489.				13. TYPE OF REPORT AND PERIOD COVERED Final; 6/79 - 2/81	
16. ABSTRACT The report summarizes results of studies of the formation of halogenated organics in chlorinated cooling waters at the Allen, Kingston, and Shawnee Steam Plants from June through December 1979. The data indicate that low levels (generally <20 ppb) of some halogenated organic compounds are formed during power plant chlorination. The chlorine dosage appears to be directly related to the level of the halogenated organics identified in the condenser cooling water system. There is no clearcut pattern that definitely supports any particular relationship between precursors (e. g. , amino acid) and halogenated organic compounds. Precursors show consistent measurements above the detection limit of the analysis techniques. Bromide, ammonia, color, and fulvic acid concentrations at the Allen Plant were clearly higher than those at the other two plants. The average humic acid concentration was similar at all plants. A temporal trend was also apparent. The amino acid data showed consistent measurement below the detection limit of the analysis techniques. The data displayed no apparent temporal trends and no obvious tendency toward one class or structural type of amino acid.				14. SPONSORING AGENCY CODE EPA/600/13	
17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
Pollution	Chlorination	Pollution Control	13B	07B	
Halogen Organic Compounds	Amino Acids	Stationary Sources		06A	
Electric Power Plants	Bromides	Halogenated Organics	07C		
Cooling Water	Ammonia	Fulvic Acid	10B	20F	
	Color		13A	08D	
	Humic Acids				
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified		21. NO. OF PAGES	
		20. SECURITY CLASS (This page) Unclassified		22. PRICE	

EPA-600/7-81-094
May 1981

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by

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Interagency Agreement No. D5-E721
Program Element No. 1NE624A

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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Washington, DC 20460

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ABSTRACT

This report summarizes the results obtained from studies to determine halogenated organic formation in chlorinated cooling waters at TVA's Allen, Kingston, and Shawnee Steam Plants from June through December 1979. Condenser cooling water samples were collected and transported to TVA's Laboratory Branch for analysis. These samples were collected at various sites throughout the condenser cooling water system from the plant intake through the condenser outlet.

Based on the data gathered, it appears that low levels (generally <20 ppb) of some halogenated organic compounds, mainly volatile ones, are formed during power plant chlorination. Only chloroform was detected more than 90 percent of the time at any location. Three semivolatile halogenated organic compounds were detected. Chlorine dosage appears to be directly related to the level of the halogenated organics identified in the condenser cooling water system.

It was determined that precursors show consistent measurements above the detection limit of the analysis techniques. Bromide, ammonia, color, and fulvic acid concentrations were higher at the Allen Plant than the other two plants. The average humic acid concentration was similar at all plants. A temporal trend was also apparent in the data. However, there is no clearcut pattern that supports any relationship between precursors such as humic acid, fulvic acid, or amino acids and halogenated organic compounds.

Results of the amino acid data showed consistent measurement below the detection limit of the analysis techniques. The data displayed no apparent temporal trends and no tendency toward one class or structural type of amino acid.

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ACKNOWLEDGEMENTS

We would like to express our appreciation to the following TVA organizations for their support during this study:

Division of Fossil and Hydro Power

Fossil Operations - W. H. Thompson

B. E. McCuiston, Allen Steam Plant, Superintendent

L. B. Kennedy, Kingston Steam Plant, Superintendent

T. D. Womble, Shawnee Steam Plant, Superintendent

Division of Natural Resource Services

Laboratory Branch - C. W. Holley, D. G. Carpenter,

L. O. Hill, B. S. Neal, W. R. Scott, T. S. Hobbs

A special appreciation is extended to B. W. Vigon, T. B. Stanford, and M. D. Hunter of Battelle-Columbus Laboratories, Columbus, Ohio; and to the Results Sections of each steam plant for their continued cooperation and support throughout this study.

CHAPTER 1.

INTRODUCTION

Because of interest in organic contaminants and the concern as to their significance, the Environmental Protection Agency (EPA) conducted tests in cities across the country to measure the concentrations of six halogenated compounds in raw and finished waters.¹ The resulting data led to the establishment of halogenated organics on the priority pollutant list.

It has been assumed that halogenated compounds are formed as a direct result of the chlorination process used by the water treatment facilities. It is also assumed that these compounds are formed by the chlorination process used to reduce biofouling in the cooling water systems of fossil fueled and nuclear power plants.

Although not final, EPA has proposed water quality criteria for many halogenated compounds.² There are questions regarding the significant production of halogenated compounds in chlorinated cooling water systems. This report presents data regarding the formation of halogenated compounds in chlorinated cooling water systems. Table 1 lists the volatile and semivolatile halogenated compounds of concern during this study.

TABLE 1. HALOGENATED ORGANICS DETERMINED
DURING THE STUDY

Volatiles:

Chloroethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Bis-(chloromethyl)-ether¹
1,1-dichloroethylene
Trans-1,2-Dichloroethylene
1,2-Dichloropropane
1,3-Dichloropropane
Bromoform
Chloroform
Methyl Chloride
Methyl Bromide
Methylene Chloride
Carbon Tetrachloride
Chlorobenzene •
Bromodichloromethane
Trichlorofluoromethane
Dichlorodifluoromethane
Dibromochloromethane

Semivolatiles:

Base-Neutral Compounds

Hexachloroethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Bis-(2-chloroethyl)-ether
Tetrachloroethylene
2-Chloronaphthalene
2-Chloroethyl vinyl ether

-
1. This compound has been removed from the list since it is very unstable in water ($t_{1/2} = 52$ s) and would not be expected in any of these water samples.²

Table 1. (Continued)

Acidic Phenols Compounds

2-Chlorophenol
3-Chlorophenol
4-Chlorophenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
Dichlorophenol
Trichlorophenol
Tetrachlorophenol
Pentachlorophenol
Monochlorocresols
Dichlorocresols
Trichlorocresols
Tetrachlorocresols

CHAPTER II.

CONCLUSIONS AND RECOMMENDATIONS

Data on volatile and semivolatile halogenated organic compounds were obtained at three TVA power plants over a four- to six-month period in 1979. Samples were analyzed at three locations--plant intake, condenser inlet, and condenser outlet--and several times prior to, during, and following a chlorination cycle. On selected dates samples were also analyzed for a variety of precursors thought to influence the halogenated compound concentrations.

Volatile halogenated organic compounds were detected with variable frequency as a function of plant and sample location. Only seven volatile halogenated organic compounds and three semivolatile halogenated organic compounds were detected. By far chloroform, being detected at each plant in excess of 90 percent of the time, was the most frequently encountered. Other volatile halogenated organics frequently detected were bromodichloromethane and dibromochloromethane. Other volatile halogenated organics occasionally found were: 1,2-dichloroethane; trans-1,2-dichloroethylene; methylene chloride; and 1,1,1-trichloroethane. The semivolatile halogenated organic compounds detected were: 2-chloronaphthalene; 2-chlorophenol; and 1,2-dichlorobenzene. All compounds except chloroform had an average detection frequency of less than 70 percent at all plants. The highest concentration of chloroform analyzed was 18.0 $\mu\text{g/l}$ as compared to the 24-hour criteria level for fresh water (500 $\mu\text{g/l}$).

The large number of precursor categories (27 in all) necessitated some selection procedure to limit the number of categories tested for a relationship with the halogenated organic compounds. By concentrating on the current mechanistic arguments for the halogenation reaction(s) and by constructing composite variables from several precursor categories, the following subset was obtained:

- Chlorine dosage
- Free residual chlorine (inlet)
- Total residual chlorine (inlet)
- Temperature
- pH
- Bromide
- Nitrogen species
- Substrate

The value of the nitrogen species variable was calculated by adding the concentrations of ammonia-nitrogen, organic nitrogen, and amino acids. The value of substrate was obtained by summing the concentrations of humic and fulvic acids.

Most of the correlation analysis effort centered on the data obtained at the Allen Plant since this was the most extensive set. Although individual sample locations provided some insight, it was the analysis of the inlet and two outlet samples during a chlorination cycle which proved most productive.

At the inlet and outlet, time 1 and 2, some interesting relationships appear. In particular the outlet chloroform versus chlorine dosage relationship becomes important and so does the correlation between chloroform and nitrogen species. Both the positive relationship with chlorine dose and the negative relationship with nitrogen species are consistent with the currently accepted trihalomethane formation mechanism. And when controlling chlorine dosage and bromide ion effects, the original correlation is strengthened.

The pH level was significantly and negatively correlated with chloroform only when the effects of nitrogen species concentrations and chlorine dosage were removed.

A similar trend was found for bromide ion, but the results were more difficult to interpret. Control of chlorine dosage and substrate produced a positive relationship while other correlations were negative. Since a negative correlation coefficient implies an antagonistic relationship between chloroform and bromide, this result is consistent with a mechanism involving bromide oxidation by chlorine.

Substrate was correlated significantly with chloroform concentration only when the effects of chlorine dosage were removed. This was interpreted to mean that the substrate-chloroform interaction was indeed present, but strongly influenced by the substrate-dose relationship.

The effects of temperature were difficult to analyze. None of the correlations indicated a linear relationship with the data from Allen. However, combining the data across plants for the outlet location and removing the effects of other precursors produced a significant relationship. This suggests that temperature influences on chloroform concentration are masked by effects of other variables on chloroform concentrations.

It is concluded that most aspects of the current hypothesis concerning the factors affecting chloroform production during chlorination can be supported by actual field test data. Several of the relationships are masked by the effects of other variables on chloroform.

Future research should focus on a detailed study at a single plant to provide a sufficient data base to analyze without combining several sample locations. Studies should attempt to collect data while controlling the parameters of chlorine dosage and condenser cooling water flow rate.

CHAPTER III.

OBJECTIVES

This study was conducted to provide a reconnaissance of the magnitude of volatile and semivolatile halogenated organics produced in a once-through cooling water system. The objectives of this project were: (1) to determine the concentration of specific halogenated organics that exist in the plants cooling water source; (2) to identify compounds produced in the chlorination process and discharged by the plant; (3) to determine the relationship of newly formed compounds to water quality; and (4) to determine any correlation between suspected precursors with the halogenated products.

CHAPTER IV.

APPROACH

This study included three TVA fossil fuel steam plants (Allen Steam Plant, Kingston Steam Plant, and Shawnee Steam Plant) with once through cooling systems. These plants were chosen for this TVA test primarily because of the chlorine minimization studies that were conducted during 1979 at each site. Samples were collected at the following points at each plant: (1) plant intake, (2) condenser inlet, and (3) condenser outlet.

All samples were collected and analyzed for volatile and semivolatile halogenated organic compounds. The intake samples documented the compounds which were present when the cooling water entered the plant and concentrations of those compounds. Samples were collected at the inlet and outlet of the condenser to determine specific halogenated organic compounds and the concentrations produced by the plant chlorination process.

The chlorination process may be a factor contributing to the formation of halogenated organics. It is during this process that precursors present in the river source are possibly combined with chlorine to form halogenated organics. Samples were, therefore, taken during the process to determine: (1) whether the formation is instantaneous or whether there is a time interval before the formation begins; and (2) what compounds are formed and their concentrations.

Initially, samples were collected during the chlorination cycle-one sample from the inlet and several from the outlet. Analyses of these samples should help determine whether the formation of compounds is greater during any one time of the chlorination cycle. Samples were also collected after the chlorination cycle was finished to determine at what point in time the formation of halogenated organics had stopped.

Raw river water samples were collected and analyzed for precursors (Table 2) and amino acids (Table 3). The goal was to determine the presence of each class of compound and provide a semiquantitative measure of the levels of each.

Presampling preparation and sampling procedures were based on techniques set forth by the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio,³ and the Division of Natural Resources Services, Laboratory Branch. These procedures represent current state of the art, but improvements and modifications were anticipated as more experience was obtained during the study.

All samples were collected and immediately cooled to 0°-4°C by packing them in ice. The samples for volatile and semivolatile organic compounds were immediately transported to the Laboratory Branch for analysis. The samples for bromide, polyhydroxybenzenes, humic acid, fulvic acid, natural color, and amino acids were shipped to an independent research laboratory which has the capabilities to perform these analyses. The procedures used for all analyses are described in Chapter VII.

The data gathered through this effort should provide information regarding the formation of halogenated organics in a chlorinated once-through condenser cooling water system. It should also help TVA and the power industry address questions regarding the production of these compounds in power plant cooling water systems.

TABLE 2. PRECURSORS MONITORED DURING THE STUDY

Free Chlorine (Inlet) ^(a)
Free Chlorine (Outlet) ^(a)
Total Chlorine (Inlet) ^(a)
Total Chlorine (Outlet) ^(a)
Chlorine Dosage (Calculated) ^(a)
Circulating Cooling Water Flow ^(a)
Organic nitrogen ^(a)
Ammonia-nitrogen ^(a,b)
Nitrate/Nitrite ^(a)
Total Organic Carbon ^(a)
Alkalinity ^(a)
Iron ^(a)
Calcium ^(a)
Magnesium ^(a)
Hardness ^(a)
pH ^(a)
Temperature (Inlet) ^(a)
Temperature (Intake) ^(a)
Temperature (Outlet) ^(a)
Total Suspended Solids ^(a)
Specific Conductance ^(a)
Bromide ^(b)
Polyhydroxybenzenes ^(b)
Humic Acids ^(b)
Fulvic Acids ^(b)
Natural Color ^(b)

(a) Analyzed by TVA Laboratory Branch

(b) Analyzed by Battelle-Columbus Division Laboratories

TABLE 3. AMINO ACIDS MONITORED DURING STUDY

-
-
1. Alanine
 2. Arginine
 3. Asparagine
 4. Aspartic Acid
 5. Cysteine
 6. Glutamine
 7. Glutamic Acid
 8. Glycine
 9. Histidine
 10. Isoleucine
 11. Leucine
 12. Lysine
 13. Methionine
 14. Phenylalanine
 15. Proline
 16. Serine
 17. Threonine
 18. Tryptophan
 19. Tyrosine
 20. Valine
-
-

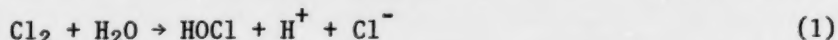
CHAPTER V.

CHEMISTRY

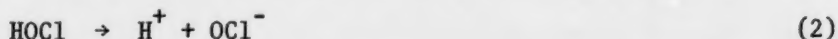
Natural waters may contain a great number of different organic materials. The extensive review of Vallentyne⁴ described thousands of compounds of widely diverse types that have been found in natural waters.

The major source of organic matter in unpolluted water supplies is plant material. This plant material can be synthetic units, metabolic intermediates, end products, or decomposition residues of the biochemical activities of members of the plant kingdom ranging from bacteria and algae to forest trees.⁵ From these sources there are many individual chemical components that may be encountered. The broad classes of chemical compounds that may be found are: carbohydrates, proteins, lipids, nucleic acids, terpenoids, carotenoids, chlorophylls, vitamins, carboxylic acids, esters, amino acids, phenolic compounds, steroids, and humic substances. The following discussion reviews the likely chlorination reactions for some diverse classes of organic compounds listed.

The central and most significant fact about aqueous chlorination, in the range of concentrations employed in water treatment, is that elemental chlorine, Cl_2 , is not involved. When chlorine is dispersed in water, Cl_2 is hydrolyzed instantaneously and completely in accord with the equation

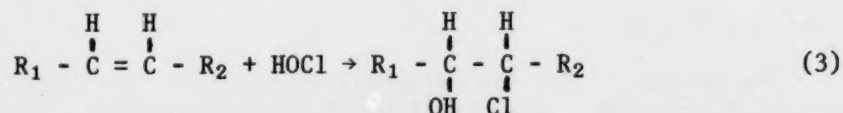


then hypochlorous acid dissociates by the following equation

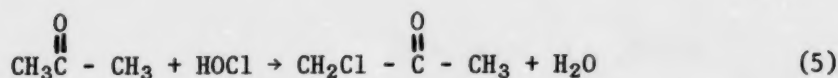
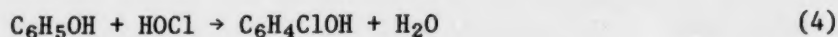


So, the reactions of hypochlorite rather than those of Cl_2 should be considered in describing the potential interactions of dilute aqueous chlorine with organic compounds. There are four principal types of reactions of hypochlorite with organic matter in aqueous solutions. These are:

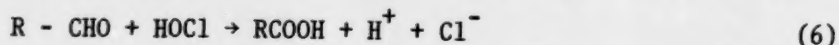
(1) Addition^{5,6}



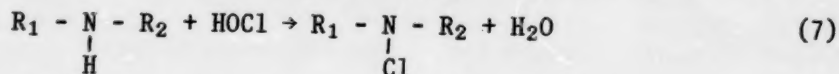
(2) Substitution^{5,6}



(3) Oxidation, with reduction of the hypochlorite chlorine to chloride^{5,6}



(4) Substitution of chlorine for hydrogen on a nitrogen atom^{5,6}



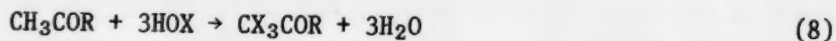
In reactions 1 and 2, formation of the chlorinated derivative is preceded by an ionization and formation of a nucleophile (C⁻) to which the positive chlorine of the hypochlorite in (OCl)⁻ becomes attached.^{7,8}

The first three types of reactions convert the chlorine either to chloride ion or to a covalently bound state in which the chlorine no longer acts as an oxidizing agent toward readily oxidized materials. These reactions may be considered part of the chlorine demand, which may be described as the conversion of active chlorine to a non-oxidizing form.⁵

The most important organic materials in natural waters are the humic and fulvic acids, which account for about 90 percent of the dissolved organic carbon in most waters. These compounds have been hypothesized as being responsible for the formation of halogenated organics.

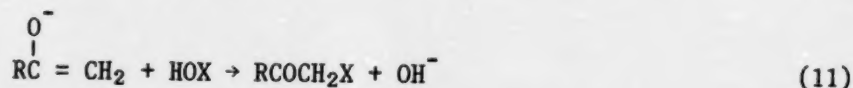
From these organic acids, trihalomethanes, such as chloroform (CHCl₃), are produced.⁶ One reaction pathway for the formation of the trihalomethanes is the haloform reaction. This reaction generally occurs in alkaline aqueous solutions with organic compounds containing the acetyl

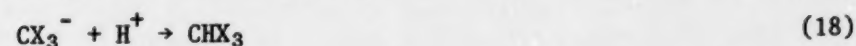
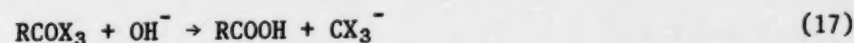
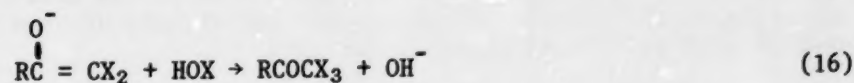
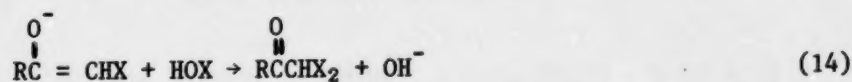
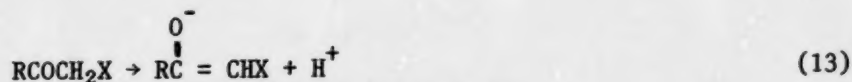
group, $\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{C}} -$, or with structures such as CH_3CHOH -that may be oxidized to the acetyl group. The three hydrogens of the methyl group are replaced by three halogen atoms and the carbon bond to the carbonyl group is split giving rise to a haloform and a carboxylic acid. This reaction may be written:



where x = Cl, Br, F, or I.

The mechanism for the halogenation reaction is an initial proton dissociation from the alpha carbon which yields an enolate carbanion which is then subject to electrophilic attack by HOCl or OCl. Subsequent dissociation and addition of positive halogen continue until full halogenation is achieved. A nucleophilic base attack displaces the CX₃ group, which combines with H⁺ to give the haloform.⁵ The mechanisms for these reactions are:





Ethanol, acetaldehyde, methyl ketones, and secondary alcohols with the general formula CH_3CHOHR are among the compounds or classes of compounds that give the haloform reaction. Thus, sources of haloforms are very extensive.

Chlorine chemistry has shown that chlorine is consumed through complex sequential and parallel reaction pathways leading to both desirable and undesirable reaction products.^{9,10} These undesirable products are the trihalomethanes (THM's). The formation of these trihalomethanes is not well understood due to the complexity of the reactions between chlorine and organic constituents in natural water.^{9,10} The rates of these reactions are generally unknown.

In view of the lack of knowledge on the rates of the multiple reaction pathways, kinetic models of THM formation have not yet been developed.⁹ Until such time the kinetic models can be developed, the quantitative understanding and control of the formation of THM's will be limited.

CHAPTER VI.

POWER PLANT DESCRIPTIONS

Each of the three plants studied is located near different cooling water sources. The Allen Plant is located on a tributary to the Mississippi River near Memphis, TN; the Shawnee Plant is located on the Ohio River just west of Paducah, KY; and the Kingston Plant is located at the confluence of the Clinch and Emory Rivers west of Oak Ridge, TN. All three plants utilize once-through condenser cooling systems. Only one unit of each multi-unit plant was sampled.

Allen Steam Plant

This plant was sampled from June 5 to December 11, 1979. During this period the following raw water characteristics were observed (Table 4).

TABLE 4. RAW WATER QUALITY AT THE ALLEN STEAM PLANT

Parameter	Maximum	Minimum	Median	Mean
pH, Std. Units	7.7	7.1	7.3	-
Total Suspended Solids, mg/l	29.0	10.0	11.0	15.0
Total Organic Carbon, mg/l	6.6	5.0	5.2	5.7
Ammonia (field), mg/l	0.32	0.02	0.05	0.12
Ammonia (lab), mg/l	0.20	0.01	0.02	0.08
Organic Nitrogen, mg/l	0.40	0.21	0.27	0.42
Chlorine Concentration, mg/l ^a	1.53	0.80	1.13	1.13
Chlorine Demand, mg/l ^b	0.63	0.31	0.46	0.47

^aCalculation for chlorine concentration is: $\frac{\text{Feed Rate lb/24 hrs}}{\text{Flow Rate gal/min}} \times 83.22 = \text{mg/l.}$

^bAfter 10 minutes.

During this monitoring period the unit load varied from 152 to 275 MW with an average of 207 MW, and the cooling water flow varied from about 86,670 gpm to 135,580 gpm averaging 116,910 gpm. Unlike the Kingston and Shawnee plants, the Allen condenser is a two-pass condenser; that is, the water completes two trips through the condenser before being discharged to the receiving water body. The chlorination cycle lasts for 30 minutes for each unit.

Shawnee Steam Plant

The Shawnee Plant was sampled from June 12 to November 6, 1979. The intake water quality was measured for the same parameters that were monitored at Allen (Table 5).

TABLE 5. RAW WATER QUALITY AT THE SHAWNEE STEAM PLANT

Parameter	Maximum	Minimum	Median	Mean
pH, Std. Units	7.4	7.3	7.3	-
Total Suspended Solids, mg/l	39.0	28.0	34.0	34.0
Total Organic Carbon, mg/l	5.8	3.0	4.4	4.4
Ammonia (field), mg/l	0.03	0.01	0.02	0.02
Ammonia (lab), mg/l	0.02	<0.01	<0.02	<0.02
Organic Nitrogen, mg/l	0.18	0.11	0.15	0.15
Chlorine Concentration, mg/l ^a	0.75	0.61	0.68	0.68
Chlorine Demand, mg/l ^b	0.24	0.13	0.18	0.18

^aCalculation for chlorine concentration is: $\frac{\text{Feed Rate lb/24 hrs}}{\text{Flow Rate gal/min}} \times 83.22 = \text{mg/l.}$

^bAfter 10 minutes.

During the monitoring period, plant load and cooling water flows were noted. Plant unit load on the sampling dates ranged from 100 to 137 MW. Cooling water flows spanned a range of 96,670 gpm to 121,930 gpm. The chlorination cycle at the Shawnee Plant is 45 minutes per unit, which is longer than the cycles at Allen and Kingston.

Kingston Steam Plant

The third plant from which samples were obtained was the Kingston Plant. Samples were obtained from June 26 to December 18, 1979. Again, intake water quality was analyzed for a number of pertinent parameters by the TVA laboratory (Table 6).

TABLE 6. RAW WATER QUALITY AT THE KINGSTON STEAM PLANT

Parameter	Maximum	Minimum	Median	Mean
pH, Std. Units	8.0	6.9	7.5	-
Total Suspended Solids, mg/l	15.0	9.0	12.0	12.0
Total Organic Carbon, mg/l	4.1	2.0	2.4	2.7
Ammonia (field), mg/l	0.03	0.01	0.02	0.02
Ammonia (lab), mg/l	0.04	0.01	0.02	0.03
Organic Nitrogen, mg/l	0.22	0.10	0.13	0.15
Chlorine Concentration, mg/l ^a	1.13	0.79	1.04	0.99
Chlorine Demand, mg/l ^b	0.47	0.19	0.27	0.30

^aCalculation for chlorine concentration is: $\frac{\text{Feed Rate lb/24 hrs}}{\text{Flow Rate gal/min}} \times 83.22 = \text{mg/l.}$

^bAfter 10 minutes.

Cooling water flows for the generating unit sampled ranged from 103,364 gpm to 111,396 gpm with a mean of 106,294 gpm. Loads of this unit correspondingly ranged from 111 to 132 MW with an average of 124 MW. The chlorination cycle at the Kingston Plant is 30 minutes for each unit.

A comparison of the plants shows that pH is the only parameter for which there was substantial consistency. The highest value of 8.0 units was measured at Kingston, while the lowest was 7.1 at Allen. The Shawnee Plant, located on the Ohio River, exhibited the highest suspended solids concentration at 39 mg/l. High levels of both organic carbon and ammonia nitrogen were observed at the Allen Plant. The combination of these components apparently caused the observed median chlorine demand of 0.46 mg/l to be significantly higher at Allen than at either of the other two plants.

CHAPTER VII.

DESCRIPTION OF ANALYTICAL PROCEDURES, SAMPLE PREPARATION, AND SAMPLE HANDLING PROCEDURES

Precursors

This class of compounds includes the species which are available in the inlet streams and are postulated to serve as the substrates for chlorination, resulting in the formation of halogenated low molecular weight halocarbons. The organic compounds determined in this class include polyhydroxybenzenes, amino acids, and humic and fulvic acids. Also determined were the levels of Br^- , NH_3 and the natural color of the inlet water samples.

The procedures developed and applied for the determination of these precursors are outlined below.¹¹

Determination of Natural Color. The platinum-cobalt method normally used for the determination of color in natural water is based on a visual comparison between standard chloroplatinate solutions and the sample.¹² Because of the unavoidable variability inherent in making such comparisons, the method employed in this study used spectrophotometric measurement of the absorbance of each sample at 362 nm as the means of comparing samples to standard chloroplatinate solutions. As natural color depends to some extent on pH, all samples were adjusted (if necessary) and measured at a pH of 7.0 units. A Cary 118 Spectrophotometer and 1 cm silica cells were used to measure the color. Standards were prepared by dilution of a stock solution containing 1.0 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 1.264 g H_2PtCl_6 (1000 mg Pt) in 1000 ml pH=5 acetate buffer. Standards were prepared over the range 5-70 mg Pt/l in 5 mg Pt increments. Because of the nonlinearity of the spectrophotometer's response over this concentration range, these data were segmented into several linear portions, and separate standard curves were determined for each corresponding concentration range as follows:

<u>mg Pt/l</u>	<u>Slope</u>	<u>Intercept</u>	<u>Corr. Coeff.</u>
1-20	8.11105	+0.13821	0.99954
20-30	11.81882	-8.5930	0.99934
35-50	577.33428	-1894.3122	0.96710

Determination of NH_3 . The quantitation of ammonia was performed using a specific ion electrode which permits the rapid, low-level determination of NH_3 with few problems from chemical interferences or the color and turbidity of the samples.¹³ Each sample was preserved with H_2SO_4 upon collection and stored at 4°C until analyzed as follows:

- Reagents: 10 N NaOH ionic strength adjustment buffer (ISAB)
Distilled water
0.1 M NH_4Cl
- Equipment: 1 Orion Model 401 Specific Ion Meter
1 HNU ISE-10-10-00 ammonia selective electrode
- Procedure: The "liter-beaker" method was used to calibrate the meter over the range 8.5-85.0 $\mu\text{g/l}$. Samples were prepared by adding 1 ml ISAB/100 ml sample; and readings were obtained immediately after calibration, allowing 20-30 seconds for the electrode to equilibrate. Any samples which read above 85.0 $\mu\text{g/l}$ were reanalyzed after calibration of the meter over the appropriate concentration decade. (Calibration should be repeated after every 4-5 samples, or every 15 minutes.)

Standards were prepared by dilution of the NH_4Cl stock solution, and a standard curve derived from them. However, because of the non-linearity of this curve at low concentrations, only the "liter-beaker" calibration procedure was used to quantitate samples below 850 $\mu\text{g NH}_3/\text{l}$.

Determination of Br^- . Inorganic bromide was determined using a bromide ion selective electrode. The analytical procedure does not require any sample pretreatment and permits the rapid low-level quantitation of Br^- with few interferences.¹⁴ Each sample was analyzed as described below:

- Reagents: 5 N NaNO_3 (ISAB)
Distilled water
0.1 N NaBr
- Equipment: 1 Orion Model 401 Specific Ion Meter
1 HNU ISE-30-35-00 Bromide Selective Electrode
1 Orion (Model 09-02) Double Junction Reference Electrode
- Procedure: The "liter-beaker" method was used to calibrate the meter over the range 40-400 $\mu\text{g/l}$. Samples were prepared by adding 2 ml ISAB/100 ml sample, and each reading was made after allowing 30 seconds for equilibration. The meter was initially calibrated over the range 40-400 $\mu\text{g/l}$. Any samples which read outside this range were reanalyzed after calibration of the meter over the appropriate range. To correct for drift, the meter was recalibrated after every 4-5 samples, or every 15 minutes.

Standards were prepared by dilution of the 0.1 M NaBr standard solution and used to prepare a standard curve. Because of the non-linearity of

this curve at low concentrations, the "liter-beaker" method was used to calibrate the specific ion meter in order to obtain values below 800 $\mu\text{g Br}^-/\text{l}$.

Determination of Humic and Fulvic Acids. Humic and fulvic acids were extracted and concentrated from aqueous samples by adsorption of these materials on polymeric resin. These materials are distinguished primarily by the molecular weight ranges which they encompass and differences in their solubilities in dilute mineral acids.¹⁵ Beyond these characterizations, humic and fulvic materials have not been well defined. However, their interactions with polymeric adsorbents such as Amberlite XAD-2 are such that these humic and fulvic acids may be sequentially eluted and thereby separated using such organic polymers.

Prepurified XAD-2 resin beads (Supelco Cat. No. 2-0279) were further purified by 24-hour soxhlet extraction with acetone. This material was then packed into glass columns of 0.9 cm id. and washed with 10 bed volumes of 0.1 N NaOH and 10-bed volumes of deionized H_2O . A bed height of 8.9 cm was used for these columns, which resulted in resin bed volumes of 5.6 ml. This bed length was chosen because bed height vs cross-sectional area ratios greater than 14:1 reportedly results in poor adsorption efficiencies.¹⁶ The procedures used for the determination of humic and fulvic acids were as follows:

Reagents: 1 N NH_4OH in methanol

Equipment: Cary 118 Spectrophotometer

Procedure: A 500 ml aliquot of each sample was adjusted to pH of 2 with HCl, and then was passed through the XAD-2 resin column at a flow of <3.3 ml/min. (35 bed volumes/hr.) This flow allowed the humic materials to be efficiently adsorbed while maximizing sample throughput. The adsorbed fulvic acids were eluted with 40 ml of deionized water at pH of 7 units, while the humic acids were removed with 40 ml of 1.0 N NH_4OH in methanol. Each fraction was collected, diluted to 50 ml with deionized water, and quantitated at 300 nm.

Standards for humic and fulvic acids were isolated from commercially available soil-derived humic materials (supplied by Aldrich Chemicals, catalog number H1,675-2). Precipitated humic acids were removed by filtration of a 1 gm/l aqueous solution of this humic material which had been acidified to a pH of 2 units with HCl. The remaining solution of fulvic acids was lyophilized to ~10 ml, and desalted by gel filtration. The desalted concentrate was then lyophilized to dryness. Elemental analyses of the humic and fulvic acids obtained in this fashion are given below and agree with those values reported in the literature.¹⁷

	Percent Composition of Humic and Fulvic Acids				
	C	H	N	O	Ash
Humic	51.8	3.5	10.2	73.1	1.6
Fulvic	30.0	2.5	10.2	52.9	14.6

Values for oxygen were determined by difference after correction for the ash content. The ash value reported above for fulvic acid is considered normal. However, to achieve such a low value required very careful desalting to remove the large amount of inorganic salts resulting from this method of isolation of fulvic acids.

Standard curves were constructed using aqueous solutions prepared from the humic and fulvic acid standards. The slope and intercept values from these curves are presented below and were used in the quantitation of water samples examined in this study.

	<u>Slope</u>	<u>Intercept</u>	<u>Corr. Coeff.</u>
Humic Acids	31.12	-2.70	0.99882
Fulvic Acids	61.56	1.91	0.99954

Determination of Polyhydroxybenzene. The well-known reaction of phenolic compounds with FeCl_3 to yield colored complexes was the basis for the method of analysis of polyhydroxybenzenes in this study. A list of the compounds which are included in this class of analytes is as follows:

Trihydroxybenzene
Tetrahydroxybenzene
Pentahydroxybenzene
Hexahydroxybenzene

Unfortunately, most of these compounds are not commercially available. However, because of the ease with which these compounds are oxidized, it is unlikely that many of these compounds would persist in the environment and therefore would not exist as the polyhydroxybenzenes in the aqueous samples examined in this study.

These materials were to be determined as a class of compounds and as such were not isolated as individual species prior to analysis. However, humic materials would be expected to be a positive interference in this analysis. Since humic and fulvic acids were being determined separately in this study, a scheme was devised to eliminate these interfering compounds prior to the determination of the polyhydroxybenzenes.

The response of the individual members of this class of components to FeCl_3 varies significantly. As such, the response observed when applying the class analysis to aqueous samples will depend upon which polyhydroxybenzenes are present and at what concentration. A more precise description of such materials would require a determination of the individual polyhydroxybenzenes species; however, the effort was beyond the scope of this study.

The procedures used for the determination of polyhydroxybenzenes are as follows:

Reagents: 1% FeCl₃(aq).
 Equipment: Bausch and Lomb Spectronic 20
 Procedure: Samples were filtered in 10 ml aliquots through a 2 cm column of Bio Gel P-2, followed by 20 mls of 0.1 N HCl. The polyhydroxybenzenes are contained in the last 10 mls, which are treated with 4 drops of FeCl₃ solution and quantitated at 500 nm.

Standard solutions were prepared from equimolar amounts of 1,2,4-trihydroxybenzene; 1,2,3,4-tetrahydroxybenzene; and hexahydroxybenzene. The benzene-triol was obtained commercially (K and K Laboratories). However, the latter two compounds were prepared using methods reported in the literature.^{18,19} The following slope and intercept values were obtained from the curve derived from these standard solutions:

	<u>Slope</u>	<u>Intercept</u>	<u>Corr. Coeff.</u>
Polyhydroxybenzenes	30.27	0.59	0.9976

Determination of Amino Acids. The analysis of these compounds was performed using the procedures described below:

Reagents: 0.1 N HCl
 Equipment: Thermovac FD-1-DG Freeze Dryer
 Procedure: A 500 ml aliquot of each water sample is placed in a 7000 ml round bottom flask and freeze dried to approximately 50 ml. The concentrated sample is then transferred to a 100 ml flask followed by a 5 ml rinse with 0.1 N HCl, and 100 ml of deionized water. Each sample is then freeze dried to dryness, and shipped to the analytical laboratory. Prior to analysis, each freeze-dried sample was dissolved in 2 ml of pH 2.2 sodium citrate buffer and spiked with 25 nM/ml each of nor-leucine and α -amino- β -guanidino-propionic acid. Each sample was then separated by ion exchange chromatography, analyzed colorimetrically after treatment with ninhydrin reagent.

Quality Assurance. The precision and accuracy of each analytical method described above was determined by a series of replicated measurements made on samples which were spiked at known concentrations. These concentrations were selected to be within the range of those encountered in the actual water samples examined in this study. Data are presented in Tables C-2 and C-3 of Appendix C.

In order to monitor the performance of each method during the analysis of samples, spiked and blank water samples were periodically analyzed.

For NH_3 and Br^- analyses, these spiked solutions were used to calibrate the instrument before and during the analysis, and as such no data were generated.

However, for all other analyses, spiked samples were processed and their concentrations determined using the appropriate procedure. Blank samples were also analyzed for each method and consisted of the trip blanks discussed under Sampling Methods. Laboratory blanks were analyzed only if the trip blanks gave values significantly greater than the detection limit of the method.

Standard curves were prepared for at least seven different standard concentrations. Detection limits were determined using the method of Hubaux and Vos,²⁰ and established as the minimum response which might be due (within the 95 percent confidence interval) to a sample of zero analyte content.

Halogenated Organics

Determination of Volatiles.²¹ Purge and trap techniques were utilized for the analysis of the volatile halogenated organics. These techniques consisted of purging a known volume of the aqueous sample with inert gas and trapping the evolved volatile organics on a Tenax trap. Trapped organics were eluted onto the head of a gas chromatographic (GC) column, separated, and measured with an electrolytic conductivity detector. Purge-and-trap and GC conditions for this procedure are given in Table 7. The general procedures are outlined below:

TABLE 7. PURGE-AND-TRAP AND GC PARAMETERS
FOR VOLATILE HALOGENATED ORGANICS

Purge Gas	He
Purge Time	12 min
Purge Rate	60 ml/min
Purge Temperature	20-25°C
Desorption Time	7 min
Desorption Temperature	180°C
GC Carrier Gas	He
Carrier Gas Flow Rate	30 ml/min
GC Column Dimensions	6 ft x 2 mm id
GC Column Packing	0.1% SP-1000 on Carbopack C
GC Column Temperature Program	60°C to 220°C at 8°C/min and 20 min at 220°C
GC Detection	Electrolytic conductivity

Equipment: Chemical Data Systems 310 Concentrator and Tracor Model 560 Gas Chromatograph with Model 700 Hall Detector

Procedure: A 10 to 20 ml aliquot of each sample was placed in the CDS 310 concentrator. The sample was purged for 12 minutes with helium and the evolved organics trapped on the Tenax trap. The trap was heated for seven minutes at 180°C and the analytes flashed onto the GC column, separated, and measured using an electrolytic conductivity detector.

Determination of Semivolatiles.^{22, 23, 24} The semivolatile constituents were divided into two groups and analyzed accordingly. The acidic (phenols) components were determined by acid adjustment of the pH, methylene chloride extraction, and gas chromatograph analysis using electron capture detection. The base neutral species were analyzed using the same method except the sample aliquot was made alkaline before methylene chloride extraction. Extraction and sample preparation procedures were as follows:

Equipment: Hewlett-Packard Model 5840A GC/ECD.

Procedure: Adjust the pH of 1000 ml sample to approximately 2 units with H₂SO₄ and extract with 3 x 60 ml of CH₂Cl₂. The combined extract is dried over MgSO₄, decanted off, and reduced in volume to 1 ml in a Kuderna-Danish apparatus. Each sample was then "solvent exchanged" by adding 5 ml hexane and again reducing in volume to 1 ml.

Acidic semivolatile compounds, including phenols, were analyzed with a 1 percent SP-1240 DA column. The deactivation process used while preparing this column packing decreases adsorption of phenols onto the packing, thus eliminating the need for derivatization of these compounds.

Gas chromatographic conditions are summarized in Table 8 below.

TABLE 8. GC-MS PARAMETERS FOR ACIDIC SEMIVOLATILE HALOGENATED ORGANICS

Column Dimension	6 ft x 0.2 mm
Column Material	1% SP-1240 DA
Carrier Gas	5% Methane and 95% Argon
Carrier Gas Flow Rate	60 ml/min
Temperature Program	80°C to 200°C at 8°C/min and 2 min at 200°C
Detector	Electron Capture Ni63

Base-neutral semivolatile compounds were determined by GC-ECD using a 3 percent SP-2250 DB column. Gas chromatographic conditions are summarized in Table 9.

TABLE 9. GC-ECD PARAMETERS FOR NEUTRAL SEMIVOLATILE HALOGENATED ORGANICS

Column Dimension	6 ft x 2 mm
Column Packing	3% SP-2250 DB
Carrier Gas	5% Methane/95% Argon
Flow Rate	60 ml/min
Temperature Program	60°C to 270°C at 5°C/min

Quality Assurance. Accuracy and precision of the volatile and semi-volatile analytical methods were determined through the analysis of standard reference, blank, and spiked samples which were examined periodically during this study. Quality control samples were prepared and analyzed with each group of samples. In the case of the volatile compound analysis, trip blanks were also examined. Detection limits were determined from the analysis of spiked samples and established at those levels where such analysis proved satisfactory. The quality control program is described in more detail in Appendix C. Actual data are presented there.

LABORATORY BRANCH

DIVISION OF NATURAL RESOURCES SERVICES

SAMPLE HANDLING PROCEDURES FOR ORGANIC ANALYSIS - CHLORINATION STUDIES

I. Containers

A. Containers for Volatile Organics

1. 40-ml screw cap glass vials equipped with Teflon-faced silicon rubber septa and open top screw caps; Pierce Chemical Company, catalog numbers 13075, 12722, and 13219, or equivalent.

B. Containers for Semivolatile Organics

1. One-gallon amber solvent bottles with Teflon-lined caps.

II. Container Preparation

The Laboratory Branch furnished precleaned containers prepared as follows:

A. Containers for Volatile Organics

1. Wash the 40-ml vials, Teflon septa, and caps with hot detergent water.
2. Thoroughly rinse with tap water.
3. Thoroughly rinse with reagent water.
4. Heat the containers and septa in an oven at 105°C for one hour.
5. Cool to room temperature in an desiccator charged with silica gel.

B. Containers for Semivolatile Organics

1. Wash the 1-gallon amber solvent bottles and Teflon-lined caps with hot detergent water.
2. Thoroughly rinse with hot tap water
3. Thoroughly rinse with reagent water.
4. Seal with Teflon-lined caps.
5. Bottles must not be opened until just prior to filling with sample or blank water.

III. Sample Collection - If the sampling line is not continuous flow, allow discharge to flow several minutes before sampling.

A. Volatile Organics

1. Collect two 40-ml vials each time samples are collected.
2. Collect samples by slowly filling the vial just to overflowing (a convex meniscus is the desired stopping point). Avoid introducing air bubbles into the sample.
3. Using spatula, carefully add one sodium thiosulfate granule (about 3 mg) to each filled vial.
4. Using clean forceps, place the septum (Teflon side down) on the sample meniscus and seal the bottle with the screw cap.
5. Invert vial and lightly tap the lid on a solid surface to ensure that the sample has been properly sealed. The absence of entrapped air bubbles indicates a proper seal. If any bubbles are present, open the vial, add additional sample and reseal. Shake gently to ensure solubilization of thiosulfate crystal.

6. Wrap the vials in waterproof packing material, place in ice chest, cover with ice, and seal the chest.

B. Semivolatile Organics

1. Fill a 1-gallon bottle to the narrow neck with a representative sample.
2. Do not allow fingers to come in contact with the inside of caps or bottles.
3. Seal bottle with Teflon-lined caps and place in ice chest.
4. Place padding between bottles to prevent breakage.
5. Cover the sample bottles with crushed ice and seal the ice chest.

IV. Sample Identification

All samples and blanks must be accurately identified with a sample number using waterproof labels and waterproof ink. Field worksheets (form TVA 17057) must be completed including sample number, date and time of sampling, type of sample and sampling site. The field sheets should be signed by the collector and the original attached to the outside of the ice chest. A copy of the field sheet is retained by the collector as a record of sample collection.

V. Sample Delivery

Samples should be delivered to the Laboratory Branch within 24 hours after collection. Samples must be analyzed within 14 days of collection.²¹ Samples not meeting this criteria will be considered unacceptable. If recollection is impossible, data from older samples must be qualified in the laboratory report.

CHAPTER VIII.

STATISTICAL ANALYSIS

This section presents the methodology used to analyze the data rather than that used to analyze the samples. Water quality analyses were performed according to Standard Methods for the Analysis of Water and Wastewater (14th Edition) or according to currently accepted EPA procedures. With regards to precursors, where a method had to be adapted from the literature or was a nonstandard method, an extensive methodology development and quality control program was followed.²⁵

Nevertheless, the error inherent in the precursors analyses influenced the interpretation of statistical procedures as noted below. Replicate samples were analyzed by two different laboratories using comparable or similar procedures for the halogenated organic compounds. In some cases, variations were noted which were attributed primarily to sample contamination during transport and secondarily, to the fact that some of the compounds of interest, particularly methylene chloride, are commonly used industrial and laboratory solvents. Their contamination of GC supply gases and the laboratory atmosphere makes it extremely difficult to consistently achieve sub-part per billion detection limits on water samples.

Battelle-Columbus Laboratories analyzed 30 samples for halogenated organics to validate the sampling and analytical methodology used by TVA. The Battelle halogenated organics data base was not used as part of the general data base for the statistical analysis.

The TVA data base used in the study consisted of multiple sets of volatile halogenated organic analyses for each plant. Generally, eight samples per sampling date were analyzed:

- Intake prior to a chlorination cycle
- Intake following chlorination
- Inlet 5 minutes after the start of chlorination
- Outlet 5-20 minutes into chlorination* (Outlet 1)
- Outlet 10-40 minutes into chlorination** (Outlet 2)
- Outlet after completion of a chlorination cycle (Outlet 3)
- Trip blank-organic free water transported from the lab to the site and back and analyzed to determine transportation contamination
- Lab blank-organic free water taken through the analysis procedure.

The number of sampling dates for the volatile organics varied from plant to plant. The Allen plant was sampled a total of nine times between the dates of June 5 and December 11, 1979. The Kingston plant was sampled eight times between June 26 and December 18, 1979. Samples were taken at Shawnee on six occasions between June 12 and November 6, 1979.

For the precursors the data base was not as extensive. Precursors shown in Table 2 as being monitored by TVA were analyzed approximately as

*Exact times varied from 5 to 20 minutes depending on the plant.

**Times varied from 10 to 40 minutes depending on the plant.

frequently as the halogenated organic compounds. Data provided by Battelle were available as follows:

Allen	5 dates	August 21 to December 11
Kingston	5 dates	August 21 to December 18
Shawnee	2 dates	October 2 and November 6

These differences are noted because they affected the statistical analysis.

The organic compounds and precursors were coded, keypunched, and organized as separate computer files to maximize flexibility. Any subset of either file could be selected and combined into a merged file for processing. Data could be accessed by parameter, by plant, by date, by sample location or other criteria to provide the merged data set.

Prior to performing any of the hypothesis testing, the data were examined for statistical characteristics. First, a frequency distribution of values above and below the analytical detection limit was generated. Compounds detected less frequently than 70 percent at any location were deleted from further consideration due to the severe limitations this placed on the statistical tests.

Many of the halogenated organic compounds existed in concentrations below detection limits. For data analysis, these data were not considered. Consequently, the mean, median, and minimum concentrations are often higher than would be the case if detection limit or half the detection limit were used for these concentrations. Also, the standard error and standard deviation are smaller than otherwise. The effect of omitting these concentrations is not as pronounced in the analysis of the precursors with chloroform because relatively few chloroform concentrations occurred below detection limits.

DESCRIPTIVE STATISTICS

Allen Steam Plant

Halogenated Organic Compounds. The frequency tabulations showed that for this plant, six volatile halogenated compounds were detected and had the distribution shown in Table 10. With the exception of chloroform and 1,1,1-trichloroethane, the compounds did not meet the criterion of a 70 percent detection frequency.

The descriptive statistics were also informative in establishing which of the compounds should be tested further. The means, maximum, minimum, and median are shown in Table 11. Chloroform and bromodichloromethane concentrations appeared to be influenced by cooling system chlorination. Only chloroform was selected for further statistical hypothesis testing.

TABLE 10. HALOGENATED ORGANIC COMPOUND DETECTION FREQUENCY SUMMARY - ALLEN PLANT

Compound	Intake (b)	Detection Frequency, Percent (a)			Average
		Inlet	Outlet 1	Outlet 2	Outlet 3 (c)
Bromodichloromethane	11.1	77.8	77.8	77.8	11.1
Dibromochloromethane	22.2	44.4	55.6	55.6	22.2
Trans-1,2-dichloroethylene	11.1	0	0	0	0
1,2-dichloroethane	55.6	44.4	22.2	33.3	33.3
1,1,1-trichloroethane	88.9	88.9	88.9	88.9	88.9
Chloroform	100.0	100.0	100.0	100.0	100.0

(a) based on nine samples analyzed at each location, detection limit is 0.05 µg/l

(b) prior to start of chlorination

(c) after cessation of chlorination

TABLE 11. HALOGENATED ORGANIC COMPOUND DESCRIPTIVE STATISTICS - ALLEN PLANT^(a)

Compound		Intake ^(b)	Inlet	Outlet 1	Outlet 2	Outlet 3 ^(c)
Bromodichloromethane	mean	0.30	1.01	1.23	1.29	0.90
	maximum	0.30	2.10	3.00	3.10	0.90
	minimum	0.30	0.40	0.50	0.40	0.90
	median ^(e)	<0.05	0.40	0.50	0.65	<0.05
	mean ^(d)	0.06	0.79	0.96	1.01	0.12
Dibromochloromethane	mean	0.75	0.80	0.66	0.62	0.90
	maximum	1.00	1.50	1.50	1.00	1.00
	minimum	0.50	0.30	0.10	0.20	0.80
	median ^(e)	<0.05	<0.05	0.25	0.20	<0.05
	mean ^(d)	0.19	0.37	0.38	0.36	0.22
Trans-1,2-dichloro- ethylene	mean	0.06	No values above detection	No values above detection	No values above detection	No values above detection
	maximum	0.06				
	minimum	0.06				
	median ^(e)	<0.05	<0.05	<0.05	<0.05	<0.05
	mean ^(d)	0.03	0.025	0.025	0.025	0.025
1,2-dichloroethane	mean	0.13	0.23	0.15	0.17	0.13
	maximum	0.20	0.30	0.20	0.20	0.20
	minimum	0.07	0.20	0.10	0.10	0.10
	median ^(e)	<0.05	<0.05	<0.05	<0.05	<0.05
	mean ^(d)	0.08	0.11	0.05	0.07	0.06
1,1,1-trichloroethane	mean	0.99	1.40	1.11	1.19	1.33
	maximum	2.00	3.20	1.80	3.00	2.00
	minimum	0.10	0.50	0.40	0.40	0.50
	median ^(e)	0.25	1.00	0.90	0.80	1.05
	mean ^(d)	0.88	1.25	0.99	1.06	1.18
Chloroform	mean	0.53	5.74	5.82	6.63	0.77
	maximum	2.90	10.00	11.00	11.00	4.40
	minimum	0.05	0.40	0.40	0.40	0.20
	median ^(e)	0.09	5.00	5.15	6.25	0.25
	mean ^(d)	0.53	5.74	5.82	6.63	0.77

(a) data exclude less than detection values except as noted; all values are expressed as µg/l

(b) prior to chlorination

(c) after the cessation of chlorination

(d) mean of all data where less than detection values are set equal to DL/2

(e) all data.

Precursors. Detection frequencies for water quality data and precursors (bromide, pH, substrate) were not calculated because there were no cases where the detection frequencies percentages were less than 100 percent.

The descriptive statistics are shown in Table 12. In comparison with the other plants the chlorine dosage, substrate concentrations, and temperatures are more favorable to chloroform production. Free residual chlorine, nitrogen species, and bromide are less favorable assuming the proposed mechanistic hypothesis is accurate.

Kingston Steam Plant

Halogenated Organic Compounds. Table 13 shows the detection frequencies for this plant. Only five volatile halogenated compounds were detected of 21 measured. They were Bromodichloromethane, Dibromochloromethane, Methylene Chloride, 1,1,1-Trichloroethane, and Chloroform. Methylene chloride was occasionally found while trans-1,2-dichloroethylene and 1,2-dichloroethane were not. Of the five compounds, only chloroform was detected more frequently than 70 percent at all locations and times. Bromodichloromethane was detected with better than 70 percent frequency at the inlet and the outlet during chlorination.

The descriptive statistics for Kingston are similar to those for Allen (Table 14). Chloroform concentration appears to have a definite relationship with cooling system chlorination while bromodichloromethane and 1,1,1-trichloroethane potentially are related to chlorination.

The mean and maximum chloroform concentrations at Kingston are lower than those at Allen for the inlet, outlet 1, and outlet 2 samples. This may be due to the fact that the chlorine dosages at Allen were higher. This relationship is discussed later in this section of the report.

Another trend apparent in the data was the difference between compounds with respect to the frequency of detection and the mean concentration at various locations within the system. Chloroform and bromodichloromethane, two of the trihalomethanes, behaved similarly. Concentrations at the intake were generally low indicating that only traces of these compounds were entering the plants from upstream sources. Concentrations also decreased rapidly after chlorination cycle completion indicating that the reaction is very dependent on the chlorine residual concentration.

The behavior of 1,1,1-trichloroethane was different than that of chloroform and bromodichloromethane. Concentrations at the intake were generally lower than elsewhere in the system, but following chlorination the concentration at the outlet was maintained at a level only slightly lower than during chlorination.

Possibly these differences in the behavior of specific compounds are explainable on the basis of different reaction mechanisms and/or different substrates.²⁶

TABLE 12. PRECURSORS - DESCRIPTIVE STATISTICS - ALLEN PLANT^(a)

Parameter	Mean	Minimum	Maximum	1.96 Sigma Limits About the Mean
Chlorine Dosage, mg/l	1.23	0.80	2.10	0.89 to 1.57
pH, standard units	-	7.10	7.70	7.22 to 7.51
Bromide, µg/l	278.12	95.80	670.00	14.33 to 570.57
Nitrogen Species, µg/l	459.94	266.20	728.10	319.40 to 600.49
Free Residual Chlorine, mg/l	0.17	0.09	0.23	0.13 to 0.21
Total Residual Chlorine, mg/l	0.40	0.16	0.65	0.28 to 0.53
Substrate, mg/l	2.12	0.70	3.00	1.02 to 3.22
Intake Temperature, °F	73.58	51.80	87.60	64.68 to 82.48
Inlet Temperature, °F	72.80	46.00	87.60	62.72 to 82.88
Outlet Temperature, °F	86.68	54.00	100.00	75.48 to 97.87

(a) Values measured at intake except chlorine residuals at inlet and temperature as noted.

TABLE 13. HALOGENATED ORGANIC COMPOUND DETECTION FREQUENCY SUMMARY - KINGSTON PLANT

Compound	Intake (b)	Detection Frequency, Percent (a)			Outlet 3 (c)	Average
		Inlet	Outlet 1	Outlet 2		
Bromodichloromethane	12.5	100.0	100.0	87.5	0	60.0
Dibromochloromethane	0	12.5	25.0	25.0	0	12.5
Methylene Chloride	12.5	12.5	12.5	12.5	12.5	12.5
1,1,1-trichloroethane	37.5	50.0	50.0	50.0	37.5	45.0
Chloroform	75.0	100.0	100.0	100.0	75.0	90.0

(a) based on eight samples analyzed at each location, detection limit is 0.05 µg/l

(b) prior to start of chlorination

(c) after cessation of chlorination

TABLE 14. HALOGENATED ORGANIC COMPOUND DESCRIPTIVE STATISTICS - KINGSTON PLANT^(a)

Compound	Intake (b)	Inlet	Outlet 1	Outlet 2	Outlet 3 (c)
Bromodichloromethane	mean	0.40	0.44	0.65	0.73
	maximum	0.40	0.60	1.00	0.60
	minimum	0.40	0.30	0.40	1.00
	mean (d)	0.07	0.44	0.65	0.64
Dibromochloromethane	mean	no	0.08	0.49	0.09
	maximum	values	0.08	0.90	0.09
	minimum	above	0.08	0.08	0.08
	mean (d)	0.025	0.03	0.14	0.04
Methylene chloride	mean	1.10	60.00 ^(e)	16.00 ^(e)	5.00
	maximum	1.10	60.00	16.00	5.00
	minimum	1.10	60.00	16.00	5.00
	mean (d)	0.16	7.52	2.02	0.65
1,1,1-trichloroethane	mean	0.17	0.48	0.40	0.38
	maximum	0.20	0.70	0.60	0.60
	minimum	0.10	0.30	0.20	0.20
	mean (d)	0.08	0.25	0.21	0.20
Chloroform	mean	0.14	3.83	4.76	4.45
	maximum	0.30	6.30	7.20	5.40
	minimum	0.07	2.10	3.00	3.60
	mean (d)	0.11	3.83	4.76	4.45

(a) data exclude values less than detection except as noted; all values are µg/l

(b) prior to chlorination

(c) after the cessation of chlorination

(d) mean of all data where less than detection values are set equal to DL/2

(e) data point outside the 95 percent confidence interval when less than detection values are included; suspected contamination.

Precursors. The precursor data summary for this plant shows that with respect to bromide and nitrogen species, the formation of trihalomethanes is favored (Table 15). However, the chlorine dosage and the substrate concentrations were less conducive to trihalomethane production.

Shawnee Steam Plant

The data base for this plant was more limited than that for the other two plants. Comparisons between the Shawnee data and that of the other plants should be made with caution.

Halogenated Organic Compounds. The detection frequency summary for this plant shows that only chloroform was detected in a manner consistent with the other plants (Table 16). The other compound detected with greater than 70 percent frequency at all locations was 1,2-dichloroethane. While this compound was detected irregularly at the Allen Plant, and never at Kingston, Shawnee detection frequencies were never less than 100 percent. Why the difference for this particular compound was observed is unclear, however, the mean concentrations are indicative of only a mild plant related effect (Table 17). This compound was not subjected to further analysis.

Concentrations of bromodichloromethane where the values were initially low, increased substantially during chlorination, then rapidly dropped to low levels again. It is also interesting that formation of the dibromo compound was higher at the plants having the highest and lowest bromide ion concentrations, namely, Allen and Shawnee. This suggests that bromide ion concentration is not related to production of dibromochloromethane in a simple way.

Precursors. The data summary for precursors at this plant is shown in Table 18. Relative to the other plants the chlorine dosages were the lowest, yet the chloroform concentrations were the highest. This is probably due to interaction effects with the other variables, particularly bromide ion and nitrogen species. Shawnee also had relatively high temperature compared to Kingston which had both the lowest temperatures and the lowest chloroform concentrations.

STATISTICAL TESTS

The statistical analysis was performed using the Statistical Package for Social Sciences (SPSS).²⁷ Details of the procedures are available in this reference and standard statistical texts. Brief summaries of the tests are given below.

The data on the organic compounds were first screened to determine locations where detailed analyses would be done and for which compounds. The most frequently detected compound was then used for subsequent tests. Three basic procedures were used to test various hypotheses about the relationships.

TABLE 15. PRECURSORS - DESCRIPTIVE STATISTICS - KINGSTON PLANT^(a)

Parameter	Mean	Minimum	Maximum	1.96 Sigma Limits About the Mean
Chlorine Dosage, mg/l	0.88	0.60	1.13	0.70 to 1.05
pH, standard units	-	7.00	8.00	7.20 to 7.77
Bromide, µg/l	133.33	112.00	172.00	50.00 to 216.67
Nitrogen Species, µg/l	173.24	100.00	257.20	103.20 to 243.28
Free Residual Chlorine, mg/l	0.42	0.06	1.12	0.14 to 0.69
Total Residual Chlorine, mg/l	0.65	0.32	1.61	0.29 to 1.00
Substrate, mg/l	1.58	0.90	2.70	0.67 to 2.49
Intake Temperature, °F	62.77	46.40	70.00	53.85 to 71.70
Inlet Temperature, °F	64.29	46.00	73.00	54.43 to 74.12
Outlet Temperature, °F	80.43	61.00	88.00	69.05 to 91.80

(a) Values measured at intake except chlorine residuals at inlet and temperature as noted.

TABLE 16. HALOGENATED ORGANIC COMPOUND DETECTION FREQUENCY SUMMARY - SHAWNEE PLANT

Compound	Intake (b)	Detection Frequency, Percent (a)				Average (e)
		Inlet (c)	Outlet 1	Outlet 2	Outlet 3 (d)	
Bromodichloromethane	0	80.0	100.0	100.0	0	55.2
Dibromochloromethane	50.0	60.0	66.7	66.7	33.3	55.2
Trans-1,2-dichloroethylene	16.7	0	16.7	0	0	6.8
1,2-dichloroethane	100.0	100.0	100.0	100.0	100.0	100.0
1,1,1-trichloroethane	50.0	60.0	33.3	33.3	50.0	44.8
Chloroform	100.0	100.0	100.0	100.0	100.0	100.0

(a) based on six samples analyzed at each location except inlet

(b) prior to start of chlorination

(c) based on five samples

(d) after cessation of chlorination

(e) weighted to reflect fewer number of samples at inlet

TABLE 17. HALOGENATED ORGANIC COMPOUND DESCRIPTIVE STATISTICS - SHAWNEE PLANT^(a)

Compound	Intake ^(b)	Inlet	Outlet 1	Outlet 2	Outlet 3 ^(c)
Bromodichloromethane	mean	0.84	1.13	1.10	no values
	maximum	1.80	2.20	2.40	above
	minimum	0.10	0.40	0.40	detection
	mean ^(d)	0.84	1.13	1.10	
Dibromochloromethane	mean	0.28	0.30	0.30	0.20
	maximum	0.40	0.40	0.50	0.30
	minimum	0.10	0.20	0.20	0.10
	mean ^(d)	0.21	0.21	0.21	0.08
Trans 1,2-dichloroethane	mean	no values	0.20	no values	no values
	maximum	above	0.20	above	above
	minimum	detection	0.20	detection	detection
	mean ^(d)	0.025	0.05	0.025	0.025
1,2-dichloroethane	mean	5.03	6.68	6.48	5.33
	maximum	7.50	9.00	13.00	7.80
	minimum	2.60	4.60	2.70	3.70
	mean ^(d)	5.03	6.68	6.48	5.33
1,1,1-trichloroethane	mean	1.10	1.90	1.60	1.53
	maximum	3.00	3.60	3.00	4.20
	minimum	0.10	0.20	0.20	0.20
	mean ^(d)	0.56	0.65	0.55	0.78
Chloroform	mean	0.30	0.79	0.90	0.43
	maximum	0.50	7.86	9.22	0.60
	minimum	0.08	13.60	18.00	0.20
	mean	0.25	5.00	4.80	0.43
			7.86	9.90	

(a) data include values less than detection except as noted; all values are µg/l

(b) prior to chlorination

(c) after the cessation of chlorination

(d) mean of all data where less than detection values are set equal to DL 1/2

TABLE 18. PRECURSORS - DESCRIPTIVE STATISTICS - SHAWNEE PLANT^(a)

Parameter	Mean	Minimum	Maximum	1.96 Sigma Limits About the Mean
Chlorine Dosage, mg/l	0.79	0.58	1.04	0.57 to 1.00
pH, standard units	-	7.30	7.70	7.24 to 7.56
Bromide, µg/l ^(b)	107.20	46.40	168.00	
Nitrogen Species, µg/l ^(b)	186.35	150.90	221.80	
Free Residual Chlorine, mg/l	0.31	0.09	0.56	0.12 to 0.51
Total Residual Chlorine, mg/l	0.46	0.25	0.66	0.26 to 0.66
Substrate, mg/l ^(b)	1.85	1.50	2.20	-2.59 to 6.30
Intake Temperature, °F	71.60	60.80	80.60	64.04 to 79.16
Inlet Temperature, °F	75.17	60.00	85.00	65.65 to 84.68
Outlet Temperature, °F	86.58	73.50	96.00	78.29 to 94.88

(a) Values measured at intake except chlorine residuals at inlet and temperature as noted.

(b) Statistics based on only two analyses.

This first hypothesis tested was whether there was a significant change in the concentration of a particular halogenated compound as the water passed from the intake to the outlet of a given plant cooling system. Based on classical chemical kinetic theory and monitoring of free and total residual chlorine in cooling systems, it was expected that chloroform concentrations would exhibit a clear cut trend with time and location in the system. A simple examination of the data was performed by plotting location on the abscissa and chloroform concentration on the ordinate. When the data from a single sampling date are plotted they exhibit a characteristic pattern known as an umbrella curve (Figure 1).^{28,29} Concentrations at the raw water intake were characteristically low, but increased markedly at the inlet to the condenser after chlorine had been dosed into the system. At the condenser outlet there was a further tendency toward increasing chloroform concentrations as long as chlorine was still being added. However, once chlorination ceased the concentrations quickly returned to background levels.

When the data from all sampling dates were combined the resulting envelope curve shows the influences of random and chemical influences on chloroform yields (Figure 2). Plotting of concentration versus sampling date at the inlet and outlet failed to result in an identifiable pattern such as might be produced by seasonal differences in reactive substrate material (Figures 3 and 4). This does not rule out the possibility that such trends exist but may mean only that there are other factors involved as well.

The hypothesis* that there was a significant increasing and then decreasing trend was tested by means of nonparametric statistical procedure as described below. Following this test a multiple comparisons procedure was used to determine whether pairwise differences, i.e., between any two locations, were significant and if so, at what confidence level.

Model: $y_{ij} = \mu + L_j + D_i + E_{ij}$

where Y_{ij} = ppb chloroform at location j on day i

L_j = effect due to location j

D_i = effect due to day i

E_{ij} = random error (effect of all other uncontrolled factors affecting chloroform concentration except location and day) associated with measurement at location j on day i .**

*This hypothesis was based on prior expectations of what occurs in a chlorination cycle, rather than being based on the data at hand.

**"Location" really is a combination of location and time (e.g., OUT 12 and OUT 24).

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LOCATION AND TIME AFTER CHLORINATION

Figure 1. Chloroform - Concentration Versus Location

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8:42 THURSDAY, JUNE 5, 1980 1

ALLEN STEAM PLANT
LOCATION AND TIME AFTER CHLORINATION=INL12

PLOT OF CHLOROFORM-MONTHDAY LEGEND: A = 1 OBS, B = 2 OBS, ETC.

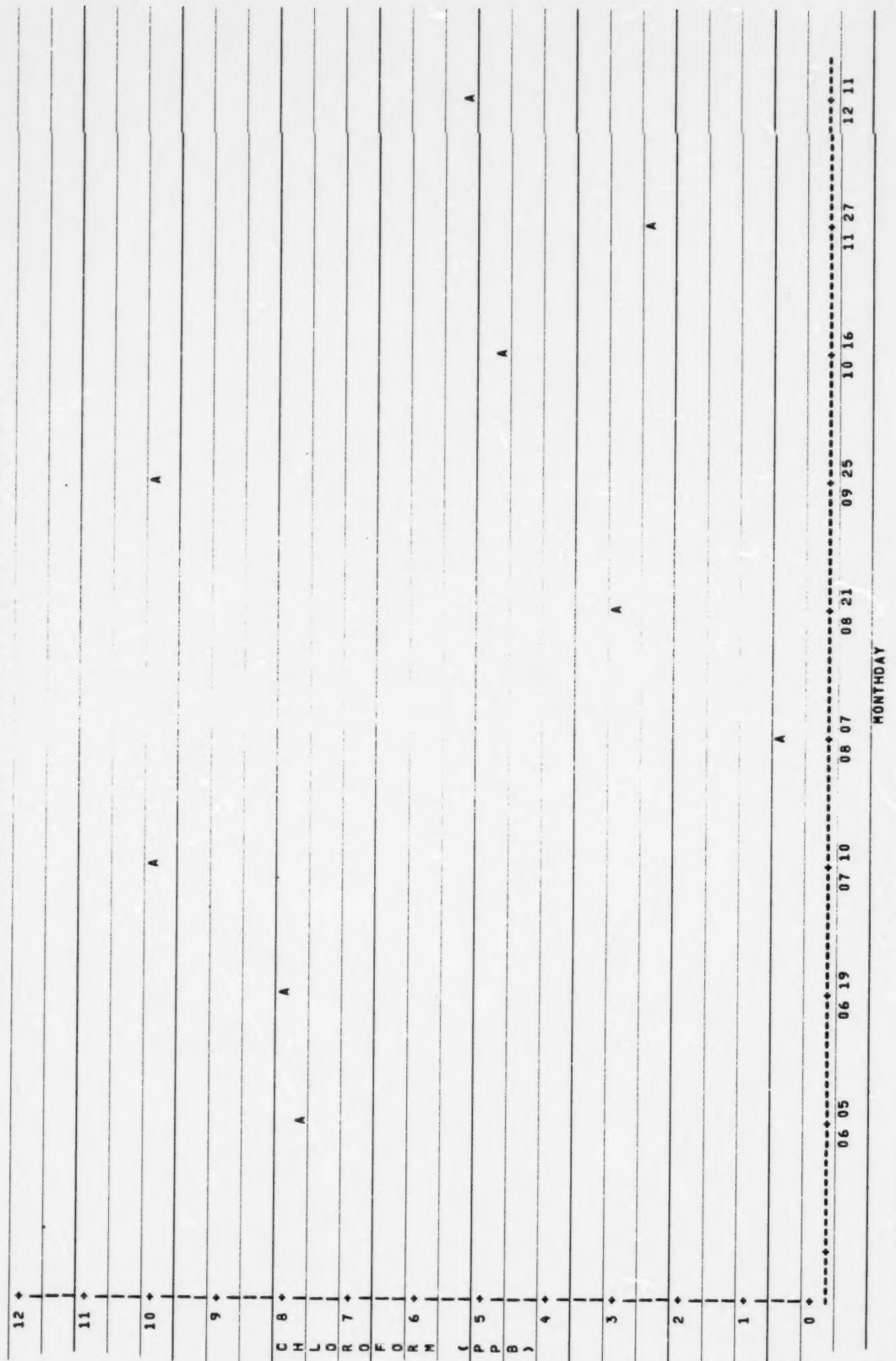


Figure 3. Chloroform Versus Month/Day For Inlet 12 Minutes

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ALLEN STEAM PLANT
LOCATION AND TIME AFTER CHLORINATION=OUT12

PLOT OF CHLOROFORM MONTHDAY LEGEND: A = 1 OBS, B = 2 OBS, ETC.

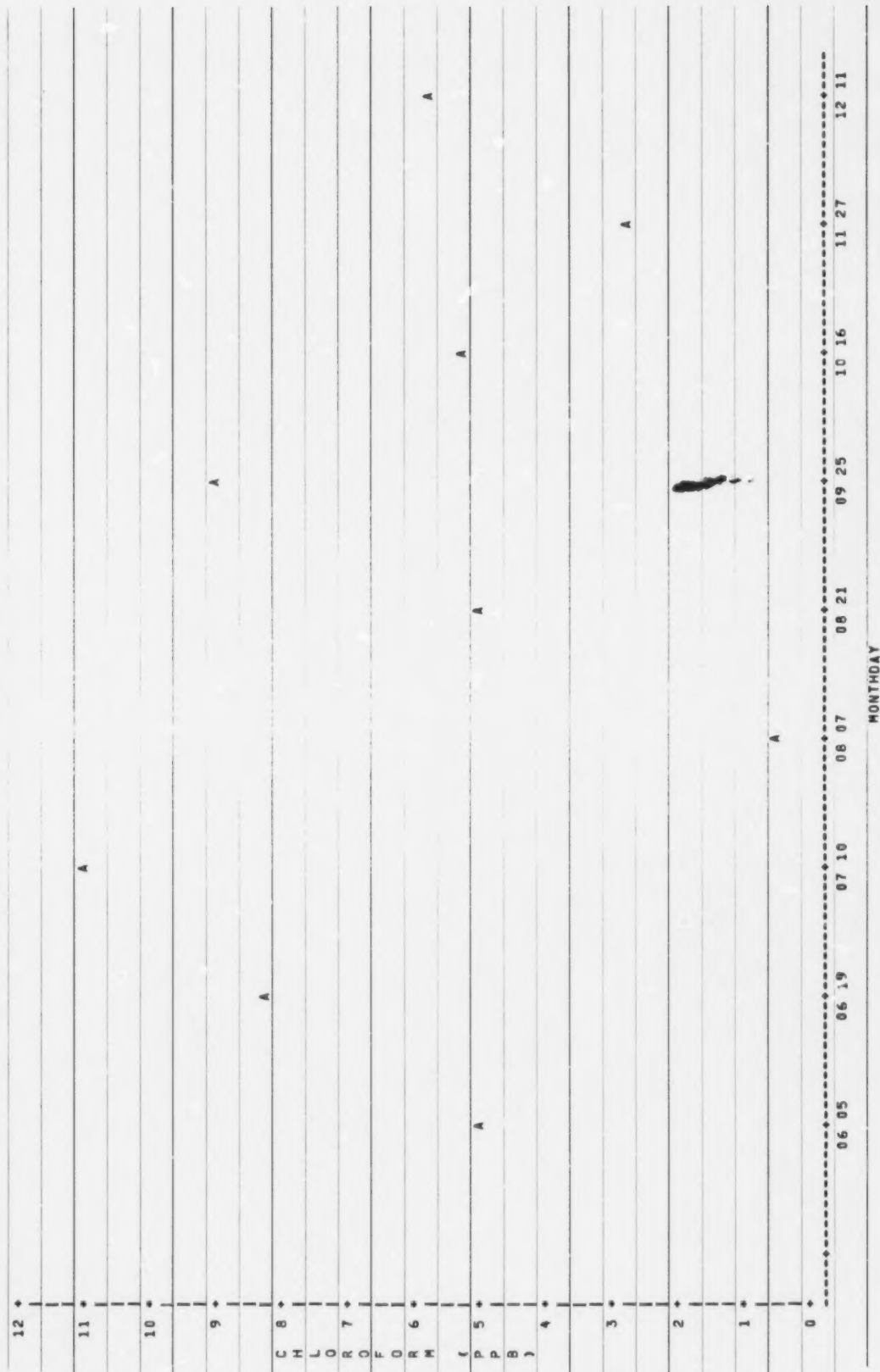


Figure 4. Chloroform - Concentration Versus Month/Day For Outlet 12 Minutes

Assume that the errors, E_{ij} , are all independent random variables having the same (but arbitrary) continuous distribution. We want to test initially the hypothesis:

$H_0: L_1 = \dots = L_5$ (i.e., there is no true difference in chloroform concentration at the various locations)

versus

$H_a: L_1 \leq \dots \leq L_\ell > \dots > L_5$, for some ℓ , $1 \leq \ell \leq 5$ (i.e., there is an increase in chloroform concentration up to some location (unknown); then (perhaps) a decline.

Procedure: (ℓ unknown procedure for block designs)

- (1) Rank the observations for each day from smallest (rank 1) to largest (rank 5). Use average ranks if two or more observations are tied.
- (2) Sum the ranks assigned to each location. Estimate the location with highest chloroform concentration values corresponding to the largest sum of ranks.
- (3) Count the number of pairs of observations increasing up to the third location and also count the number of pairs decreasing after the third location. (Used to determine whether a significant up-down trend exists.)

- (4) Standardize A_3 to get the test statistic A_ℓ^* .

This is followed by the multiple comparisons test.³⁰ The tests are approximate.

Declare $L_j \neq L_t$ if $|R_j - R_t| >_{q(.05, 5, \infty)} \left[\frac{nk(k+1)}{12} \right]^{\frac{1}{2}} \geq 18.30$

($\alpha = 0.05$)

Declare $L_j \neq L_t$ if $|R_j - R_t| >_{q(.01, 5, \infty)} \left[\frac{nk(k+1)}{12} \right]^{\frac{1}{2}} \geq 21.83$

($\alpha = 0.01$)

With this procedure it is possible to test for differences between two sets of data for continuous variables. The application to observed chloroform concentrations at the intake, inlet, and outlet of each plant's cooling system is described in the results.

The second hypothesis tested was that there was a relationship, not necessarily causal, between the levels of organic compounds measured at various points in the cooling system and certain of the precursors. The problem was twofold. First, most of the organic compounds were not

detected above the analytical threshold of 0.05 ppb. This meant that there was no variation in the concentrations which could be matched against variations in the precursors to test for a relationship. Second, the large number of precursors would result in an astronomical number of combinations if each one were tested individually. This problem is complicated by the necessity of testing the precursors against each other to identify the degree of correlation in the data set. Any inferences regarding causality must be adjusted for possible side-effects of this nature.

The approach selected was to use existing mechanistic hypotheses about the factors involved in the chlorination or bromination reaction and concentrate on supporting or refuting them. Few studies have been conducted on the factors affecting the levels of product compounds in other than a completely controlled experiment and fewer still have been attempted for a power plant system.

The present working hypothesis for the chlorination reaction involves the attack of hypochlorous acid or hypochlorite anion on naturally occurring humic and fulvic acids. This reaction is thought to be pH dependent being favored at alkaline pH, possibly due to deprotonation of the hypochlorous acid and/or the humic/fulvic acid complex and enhancement of mass transport limited reaction kinetics.

The use of partial correlation analysis was selected for the following reasons:

- (1) both simple and complex relationships could be handled,
- (2) the effects of confounding variables could be removed,
- (3) the reduction in the number of degrees of freedom for each partial correlation level was tolerable,
- (4) the direction and strength of each relationship could be obtained from the partial correlation coefficients,
- (5) the significance levels of the correlation could be estimated from t-tests of the hypothesis that the correlation coefficient was significantly different from zero.²⁷ Note: Due to correlation effects the significance levels may be somewhat lower than reported.

Following is a brief discussion of partial correlation analysis. More complete treatment of the subject is given in Nie²⁷ and Ostle.³¹

As mentioned above partial correlation provides a measure of the association between two variables while simultaneously controlling for the effects of one or more other variables. Partial correlation is based on the assumption that the relationship between the control variable(s) and both the independent and dependent variables is linear. While this may seem like a stringent restriction, it is no more so than the attempt to fit a linear multiple regression to untransformed data.

Partial correlation coefficients may be considered as being constructed by statistically calculating new dependent and independent variables with the effects of the control variable(s) removed. This is done by predicting (from the simple correlation coefficient) the dependent and independent variables from the knowledge of the effects of the control variable. The new variable is constructed by taking the difference between the actual value of the original independent variable (for each observation) and its value as predicted by the control variable. The new variables are not correlated at all with any of the controls and therefore the correlation represents the association with the confounding effects removed. However, rather than actually calculating new variables, the computation can be accomplished by using the basic formula:

$$r_{ij,k} = \frac{r_{ij} - (r_{ik})(r_{jk})}{\sqrt{1 - r_{ik}^2} \sqrt{1 - r_{jk}^2}}$$

where k is the index for the control variable, and i and j are, respectively, the indices for the independent and dependent variables. Extension to multiple control variables is relatively straightforward.

As with linear regression analysis, a partial correlation analysis cannot distinguish between a nonexistent relationship and one which is simply nonlinear. That is, a nonsignificant correlation coefficient cannot be taken to mean that the variables in question are not related, but only that no linear effect is observed.

The partial correlation coefficients were calculated for each of the variables thought important in the reaction producing chloroform. Coefficients were calculated for each plant, each location, and each time individually and for certain combinations of plants, locations, and times.

Combinations of data collected at the condenser outlet were pooled and treated as independent populations. This treatment was necessitated by the small sample size. Consequently, the intent of the partial correlation analysis is not to draw definitive conclusions about the influences of independent variables on chloroform yield. Rather the findings should be indicative of which relationships appear to be promising for future research efforts. Confidence levels of the pooled data were distorted by the treatment as noncorrelated and, therefore, are not given in the results.

Once the significant relationships had been identified, simple linear regressions and bivariate scatter diagram plots were run to establish the most basic cause-effect relationships. For the reasons mentioned previously, and because the relations are actually much more complex than the simple regressions allow, too much importance should not be placed on this portion of the study.

The following section discusses the results of the research, beginning with a description of the data base and the distributional characteristics at each location, plant, and time. This is followed by the analysis of within plant locational differences in chloroform concentrations and the identification of the important related factors. Finally, the scattergram plots and simple regressions are presented.

Following are the results obtained from the statistical analysis of the cooling water samples. The results from the Allen Plant are discussed first, followed by those from Kingston Plant, and finally those from Shawnee.

The semivolatile halogenated organic compounds were below detection limits on all dates for all plants with three exceptions. At Allen Steam Plant on September 25 and November 27, 1979, 2-chlorophenol was detected. At Kingston Steam Plant on September 11, 1979, 2-chloronaphthalene and 1,2-Dichlorobenzene were detected. These data are presented in Appendix A.

Because similar concentrations at the intake, condenser inlet, and condenser outler were observed, no further analysis of the semivolatile halogenated organic compounds is offered or felt necessary.

Locational Trends in Chloroform Concentrations

Trends in the chloroform measurements were tested for significance levels using the nonparametric umbrella curve and multiple comparison test^{28,29} as described previously. This section of the report discusses these results.

Overall Trend in Data

The test that the data follow an umbrella shaped curve produced the following results:

- (1) Rank the observations for each day from smallest to largest. Ranks are given in parenthesis.

LOCATION (L)					
Chloroform	Int 00	Inlet 12	Outlet 12	Outlet 24	Outlet 35
1	2.90(1)	7.80(4)	4.90(3)	10.00(5)	4.40(2)
2	.50(1)	8.00(4)	8.30(5)	7.80(3)	.60(2)
3	.50(1.5)	9.90(3)	11.00(4.5)	11.00(4.5)	.50(1.5)
4	.50(5)	.40(3.5)	.40(3.5)	.30(1.5)	.30(1.5)
5	.05(1)	3.10(3)	5.00(4)	7.20(5)	.20(2)
6	.08(1)	10.00(4.5)	9.00(3)	10.00(4.5)	.20(2)
7	.08(1)	4.80(3)	5.30(5)	5.20(4)	.30(2)
8	.10(1)	2.50(3)	2.70(4.5)	2.70(4.5)	.20(2)
9	.08(1)	5.20(3)	5.80(5)	5.50(4)	.20(2)

- (2) Sum the ranks assigned to each location

$$R_1 = 13.5 \quad R_2 = 31.0 \quad R_3 = 37.5 \quad R_4 = 36.0 \quad R_5 = 17$$

Location 3 has the largest sum of ranks.

- (3) Count the number of pairs of observations increasing up to the third location and also count the number of pairs decreasing after the third location.

$$A_3 = 4 + 6 + 5.5 + 3 + 5 + 4 + 6 + 5.5 + 6 = 45$$

- (4) Standardize A_3 to get

$$\hat{A}_3^* = \frac{45-27}{4.743} = 3.80^*$$

- (5) Compare $\hat{A}_3^*$ to table of distribution of A_3

Therefore the initial H_0 hypothesis of no trend is rejected in favor of the alternative at the $\alpha < 0.01$ significance level.

Pairwise Comparisons

The multiple comparisons test results are given below:

Locations	$ R_j - R_t $	Approximate Procedure (large N)		Procedure (Exact)	
		$\alpha = .05$ Critical Value	$\alpha = .01$ Critical Value	$\alpha = .037$	$\alpha = .008$
12	17.5	18.30	21.83	19	22
13	24.0	"*	"*	"*	"*
14	22.5	"*	"*	"*	"*
15	3.5	"	"	"	"
23	6.5	"	"	"	"
24	5.0	"	"	"	"
25	14.0	"	"	"	"
34	1.5	"	"	"	"
35	20.5	"*	"	"*	"
45	19.0	"*	"	"*	"

Declare: $L_1 \neq L_3$ at $\alpha = .01$ level
 $L_1 \neq L_4$ at $\alpha = .01$ level
 $L_5 \neq L_3$ at $\alpha = .05$ level
 $L_5 \neq L_4$ at $\alpha = .05$ level

Locations (in increasing
order)
1 5 2 4 3

*Indicates a significant difference at the α -level given at the top of the corresponding column.

Increases in chloroform were most significant between the intake and the outlet during chlorination. There was a significant difference at the 99 percent confidence level. At the 95 percent confidence level the differences between the outlet during and after chlorination are significant. If a 90 percent significance level is acceptable, the differences between the intake and inlet are significant.

FACTORS RELATED TO CHLOROFORM PRODUCTION

This section of the report is an analysis of the relationships between chloroform concentration and a selected subset of precursors. The results are presented at two levels. The first of the relationships tested was a simple bivariate correlation between each of the variables. The correlation coefficients were then tested for significance. The associated significance levels are for the hypothesis of no correlation among the variables.

The second level was a partial correlation of each precursor against chloroform, controlling for the effects of one other precursor and pairwise correlations controlling for two other precursors. Due to data limitations this process could not be carried to its logical conclusion of controlling for as many effects as possible, particularly when the data from a single sample location was used.

Allen Steam Plant

The data base for the analysis at Allen is the most extensive and hence the results for this plant are the most important. Tables 19 through 23 are matrices showing the simple (zero order) partial correlation coefficients, and the number of degrees of freedom for the intake, inlet, outlet at time 1, outlet at time 2, and outlet at time 3, respectively.

At the intake (Table 19) most of the relationships are not particularly significant. None of the environmental precursors--pH, bromide, nitrogen species, or substrate--shows a significant relationship with intake chloroform concentrations. Substrate concentration versus chloroform concentration has a very high coefficient of 0.948, but more than the three degrees of freedom available would be needed to show whether the relationship is significant.

Chlorine dosage and temperature (intake) were also not significantly correlated with chloroform concentrations. With respect to chlorine dosage this is expected since chlorine dosage would be independent of the background chloroform concentrations in any case. However, free and total residual chlorine exhibited negative correlations. These relationships must be spurious since chlorine is not even present in the cooling system at the intake. Their mutual variation in concentration must be coincidental.

The lack of a relationship with ambient temperature ($r=0.0572$, D.F. = 3), suggests only that ambient seasonal temperatures vary randomly or nonlinearly with background chloroform concentrations, or that, by chance, a truly linear relationship was not observed in this particular round of sampling.

At the inlet and outlet, time 1 and 2, some interesting relationships appear. In particular the outlet chloroform versus chlorine dosage relationship becomes important and so does the correlation between chloroform and nitrogen species. Both the positive relationship with chlorine dose and the negative relationship with nitrogen species are consistent with the currently accepted trihalomethane formation mechanism.

TABLE 19. SIMPLE CORRELATIONS, ALLEN, INTAKE

----- P A R T I A L C O R R E L A T I O N C O E F F I C I E N T S -----						
	CHLORO1	CLDOSAGE	FRCIN	TRCIN	pH	BRS
						NSPECIE
						SUBSTRAT
CHLORO1	1.0000 (0) P=*****					
CLDOSAGE	-.1560 (6) P= .356	1.0000 (0) P=*****				
FRCIN	-.5588 (6) P= .075	.6682 (6) P= .035	1.0000 (0) P=*****			
TRCIN	-.6370 (6) P= .045	.2330 (6) P= .289	.5638 (6) P= .073	1.0000 (0) P=*****		
pH	-.1185 (6) P= .390	.6066 (5) P= .074	.1587 (5) P= .367	-.3547 (5) P= .217	1.0000 (0) P=*****	
BRS	-.2506 (3) P= .500	.1156 (3) P= .500	.2230 (3) P= .500	-.7103 (3) P= .500	.2089 (2) P= .500	1.0000 (0) P=*****
NSPECIE	.0343 (7) P= .465	.0377 (6) P= .465	-.2962 (6) P= .238	.3606 (6) P= .190	-.1025 (6) P= .405	1.0000 (0) P=*****
SUBSTRAT	.9484 (3) P= .500	-.8946 (3) P= .500	-.2549 (3) P= .500	.6437 (3) P= .500	-.8804 (2) P= .500	.6701 (3) P= .500
						1.0000 (0) P=*****

TABLE 20. SIMPLE CORRELATIONS, ALLEN, INLET

----- PARTIAL CORRELATION COEFFICIENTS -----								
	CHLOR01	CLDOSAGE	FRCIN	TRCIN	pH	BRS	NSPECIE	SUBSTRAT
CHLOR01	1.0000 (0) P=*****							
CLDOSAGE	.3940 (6) P= .167	1.0000 (0) P=*****						
FRCIN	.5280 (6) P= .089	.6682 (6) P= .035	1.0000 (0) P=*****					
TRCIN	.0089 (6) P= .492	.2330 (6) P= .289	.5638 (6) P= .073	1.0000 (0) P=*****				
pH	-.0976 (6) P= .409	.6066 (5) P= .074	.1587 (5) P= .367	-.3547 (5) P= .217	1.0000 (0) P=*****			
BRS	-.0086 (3) P= .500	.1156 (3) P= .500	.2230 (3) P= .500	-.7103 (3) P= .500	.2089 (2) P= .500	1.0000 (0) P=*****		
NSPECIE	-.4769 (7) P= .097	.0377 (6) P= .465	-.2962 (6) P= .238	.3606 (6) P= .190	-.1025 (6) P= .405	-.6772 (3) P= .500	1.0000 (0) P=*****	
SUBSTRAT	.0991 (3) P= .500	-.8946 (3) P= .500	-.2549 (3) P= .500	.6437 (3) P= .500	-.8804 (2) P= .500	-.4128 (3) P= .500	.6701 (3) P= .500	1.0000 (0) P=*****

TABLE 21. SIMPLE CORRELATIONS, ALLEN, OUTLET, TIME 1

----- P A R T I A L C O R R E L A T I O N C O E F F I C I E N T S -----								
	CHLOR01	CLDOSAGE	FRCIN	TRCIN	pH	BRS	NSPECIE	SUBSTRAT
CHLOR01	1.0000 (0) P=*****							
CLDOSAGE	.7038 (6) P= .026	1.0000 (0) P=*****						
FRCIN	.8575 (6) P= .003	.6682 (6) P= .035	1.0000 (0) P=*****					
TRCIN	.2886 (6) P= .244	.2330 (6) P= .289	.5638 (6) P= .073	1.0000 (0) P=*****				
pH	.0922 (6) P= .414	.6066 (5) P= .074	.1587 (5) P= .367	-.3547 (5) P= .217	1.0000 (0) P=*****			
BRS	.0795 (3) P= .500	.1156 (3) P= .500	.2230 (3) P= .500	-.7103 (3) P= .500	.2089 (2) P= .500	1.0000 (0) P=*****		
NSPECIE	-.4928 (7) P= .089	.0377 (6) P= .465	-.2962 (6) P= .238	.3606 (6) P= .190	-.1025 (6) P= .405	1.0000 (0) P=*****		
SUBSTRAT	-.1590 (3) P= .500	-.8946 (3) P= .500	-.2549 (3) P= .500	.6437 (3) P= .500	-.8804 (2) P= .500	-.4128 (3) P= .500	.6701 (3) P= .500	1.0000 (0) P=*****

TABLE 22. SIMPLE CORRELATIONS, ALLEN, OUTLET, TIME 2

----- PARTIAL CORRELATION COEFFICIENTS -----						
	CHLOR01	CLDOSAGE	FRCIN	TRCIN	pH	BRS
						NSPECIE
						SUBSTRAT
CHLOR01	1.0000 (0) P=*****					
CLDOSAGE	.5767 (6) P= .067	1.0000 (0) P=*****				
FRCIN	.3854 (6) P= .173	.6682 (6) P= .035	1.0000 (0) P=*****			
TRCIN	-.2466 (6) P= .278	.2330 (6) P= .289	.5638 (6) P= .073	1.0000 (0) P=*****		
pH	.2041 (6) P= .314	.6066 (5) P= .074	.1587 (5) P= .367	-.3547 (5) P= .217	1.0000 (0) P=*****	
BRS	.0707 (3) P= .500	.1156 (3) P= .500	.2230 (3) P= .500	-.7103 (3) P= .500	.2089 (2) P= .500	1.0000 (0) P=*****
NSPECIE	-.5450 (7) P= .865	.0377 (6) P= .465	-.2962 (6) P= .238	.3606 (6) P= .190	-.1025 (6) P= .405	1.0000 (0) P=*****
SUBSTRAT	-.4679 (3) P= .500	-.8946 (3) P= .500	-.2549 (3) P= .500	.6437 (3) P= .500	-.8804 (2) P= .500	.6701 (3) P= .500
						1.0000 (0) P=*****

TABLE 23. SIMPLE CORRELATIONS, ALLEN, OUTLET, TIME 3

----- P A R T I A L C O R R E L A T I O N C O E F F I C I E N T S -----						
	CHLORO1	CLDOSAGE	FRCIN	TRCIN	pH	BRS
						NSPECIE
						SUBSTRAT
CHLORO1	1.0000 (0) P=*****					
CLDOSAGE	.2177 (6) P= .302	1.0000 (0) P=*****				
FRCIN	-.6123 (6) P= .053	.6682 (6) P= .035	1.0000 (0) P=*****			
TRCIN	-.6722 (6) P= .034	.2330 (6) P= .289	.5638 (6) P= .073	1.0000 (0) P=*****		
pH	-.1389 (6) P= .371	.6066 (5) P= .074	.1587 (5) P= .367	-.3547 (5) P= .217	1.0000 (0) P=*****	
BRS	.9301 (3) P= .500	.1156 (3) P= .500	.2230 (3) P= .500	-.7103 (3) P= .500	.2089 (2) P= .500	1.0000 (0) P=*****
NSPECIE	-.0524 (7) P= .447	.0377 (6) P= .465	-.2962 (6) P= .238	.3606 (6) P= .190	-.1025 (6) P= .405	1.0000 (0) P=*****
SUBSTRAT	-.0756 (3) P= .500	-.8946 (3) P= .500	-.2549 (3) P= .500	.6437 (3) P= .500	-.8804 (2) P= .500	.6701 (3) P= .500
						1.0000 (0) P=*****

The lack of a simple linear relationship with some of the other environmental variables, especially bromide and substrate, is not surprising. In fact, small sample size and negative correlation with total residual chlorine, nitrogen species, and substrate may obscure the actual relationships for bromide. Substrate is correlated with chlorine dosage, pH, and nitrogen species and controlling for these variables is necessary for any true relationship with chloroform to be revealed. With only single sample location data there were insufficient degrees of freedom to perform the partial correlations.

To circumvent this problem, the results of the sample location tests described previously were employed to pool the data in two ways:

- combination of outlet, times 1 and 2
- combination of inlet and outlet, times 1 and 2.

First, the simple correlations were run and examined to see if the basic relationships observed with the single location data sets were maintained. Table 24 shows the matrix for the outlet samples at times 1 and 2 combined. As seen, the relationships with chlorine dosage, residuals, and nitrogen species are maintained. The correlation problem still exists between independent variables.

Partial correlations, controlling sequentially for other precursors, are shown in Table 25. The effect of this procedure is to remove a common influence from the relationship between two variables.

When bromide, substrate, and nitrogen species were individually controlled for, the relationship between chlorine dosage and chloroform is strengthened. When simultaneous pairwise control is exerted, the residual relationship is almost linear.

Control variables had no influence on correlations between free residual chlorine and chloroform concentration. Total residual chlorine versus chloroform was significantly affected by only one set of control variables--pH and substrate simultaneously.

Partial correlations with pH versus chloroform were significant in only one case. When both nitrogen species and chlorine dosage were controlled for, pH was negatively correlated. This would tend to refute the hypothesis that chloroform production is favored at high pH. There is a direct effect of pH on chloroform production, but it is masked by the variation of chlorine or nitrogen species in the systems.

The test hypothesis concerning a relationship between bromide ion concentration and chloroform production was that they would be antagonistic. The results of the partial correlations, while generally producing negative coefficients, were not very significant. The exception was the case where nitrogen species and chlorine dosage were controlled; the relation was important in this case. On the other hand, control of chlorine dosage and substrate produced a positive coefficient. It is not clear why this result was obtained since the simple correlations with both substrate and nitrogen versus bromide were negative.

TABLE 24. SIMPLE CORRELATIONS, ALLEN, OUTLET, TIMES, 1 AND 2 COMBINED

----- P A R T I A L C O R R E L A T I O N C O E F F I C I E N T S -----						
	CHLORO1	CLDOSAGE	FRCIN	TRCIN	pH	BRS
CHLORO1	1.0000 (0)					
CLDOSAGE	.6283 (14)	1.0000 (0)				
FRCIN	.6048 (14)	.6682 (14)	1.0000 (0)			
TRCIN	.0130 (14)	.2330 (14)	.5638 (14)	1.0000 (0) P=*****		
pH	.1498 (14)	.6066 (12)	.1587 (12)	-.3547 (12)	1.0000 (0)	
BRS	.0739 (8)	.1156 (8)	.2230 (8)	-.7103 (8)	.2089 (6)	1.0000 (0)
NSPECIE	-.5155 (16)	.0377 (14)	-.2962 (14)	.3606 (14)	-.1025 (14)	-.6772 (8)
SUBSTRAT	-.3233 (8)	-.8946 (8)	-.2549 (8)	.6437 (8)	-.8804 (6)	-.4128 (8)
						1.0000 (0)

TABLE 25. PARTIAL CORRELATION MATRIX - ALLEN, OUTLET, TIMES 1 AND 2

Chloroform Versus	Simple	Controlling For ^(a)														
		1	2	3	4	5	1,2	1,3	1,4	1,5	2,3	2,4	2,5	3,4	3,5	4,5
Chlorine Dosage	0.628 ^(b)	0.684	0.626	0.756	0.802	-	0.685	0.876	-	-	0.952	0.973	-	-	-	-
Free Residual Chlorine	0.605	0.595	0.605	0.552	0.571	-	0.599	0.546	0.559	-	0.630	0.588	-	0.557	-	-
Total Residual Chlorine	0.013	0.072	0.093	0.249	0.305	-	0.142	0.621	-	-0.072	0.340	-	0.281	-	-	-
pH	0.149	-	0.138	0.114	-0.300	-0.374	-	-	-	-	0.223	-0.340	-0.380	-	-0.680	-
Bromide Ion	0.074	0.044	-	-0.437	-0.069	0.002	-	-0.469	-0.198	0.073	-	-	-	-0.441	-0.906	0.922
Nitrogen Species	-0.516	-0.509	-0.634	-	-0.426	-0.694	-0.649	-	-	-0.822	-	-0.581	-0.953	-	-	-
Substrate	-0.323	-0.408	-0.322	-0.0348	-	0.687	0.4448	0.075	-	-	-	-	0.959	-	-	-

(a) 1 = pH
2 = Bromide
3 = Nitrogen Species
4 = Substrate
5 = Chlorine Dosage(b) 0.0628 = r_{ij} (coefficient)

Control of other precursors, particularly bromide and chlorine dose, strengthened the relationship between chloroform and nitrogen species. The original hypothesis of a positive trend between substrate and chloroform concentration was not supported by the simple correlation or any of the partial correlations except when controlling for chlorine dosage. Since chlorine dosage and substrate were highly correlated in the simple correlation, the true relationship between substrate and chloroform concentration was obscured. Removal of the effects of chlorine dosage results in a significant positive trend between chloroform and substrate.

Partial correlations run for other sets of pooled halogenated organic data produced trends in a similar direction but weaker in terms of significance. This was expected because the homogeneity of the underlying sample distributions was not as great as the outlet, time 1 and time 2 data. Only temperature showed some interesting trends. When the data for outlet samples at all plants were combined and the effects of other precursors removed, the relationship was significant. This suggests that the temperature affects the reaction rates and the types of species present in a complex way.

Kingston Steam Plant

Only the simple correlations for the Kingston Plant, outlet, time 1, time 2, and time 3 were performed. Other locations and correlation levels were not attempted due to the small data set. Interpretation was not generally attempted due to the small data set, but the relationships for chlorine dose versus chloroform did not appear significant.

Shawnee Steam Plant

Only the simple correlations for the Shawnee Plant, outlet, time 1, time 2, and time 3 were performed. Other locations and correlation levels were not run due to the lack of data. The simple correlations for pH, bromide, nitrogen species, and substrate had too few degrees of freedom for interpretation. Chlorine dosage and residual chlorine exhibited the same trends as were observed at Allen.

SCATTERGRAMS AND LINEAR REGRESSIONS

For the Allen Plant outlet data (Figures 5 to 7) bivariate plots of chloroform versus chlorine dosage, free residual chlorine (inlet), and nitrogen species were run. These three precursors were selected because they gave the best linear fit for the correlation analysis.

Scattergrams were also plotted of the logarithm of chloroform versus the logarithm of substrate concentration (Figure 8). This transformation did not improve the relationship significantly over that of a linear fit. The second log-log plot of chloroform versus nitrogen species did improve the relationship slightly ($r_{\log} = -0.576$, $P=0.006$ versus linear = -0.516 ; $P=0.014$) (Figure 9).

FIGURE 5. SCATTERGRAM OF CHLOROFORM VERSUS CHLORINE DOSAGE

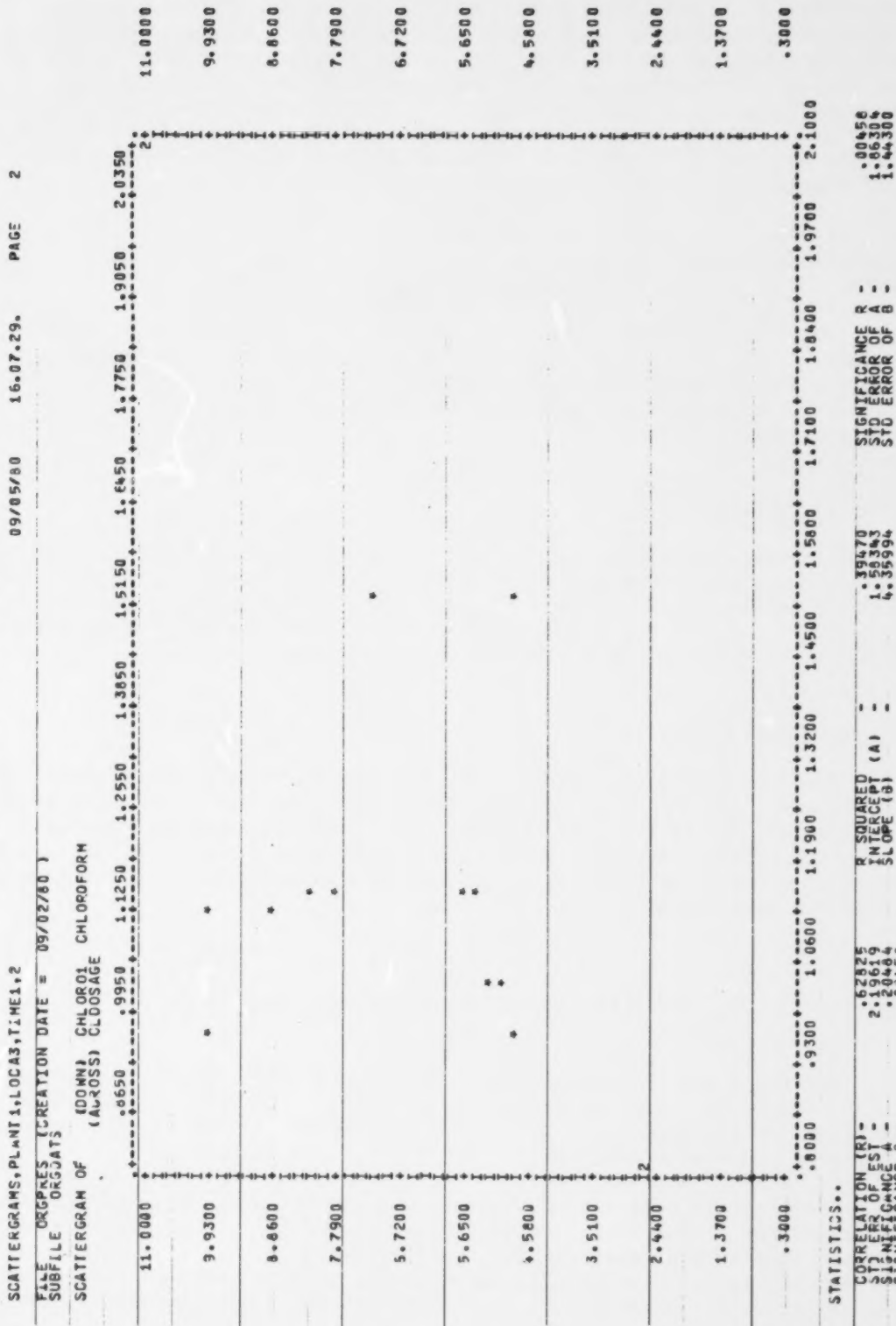
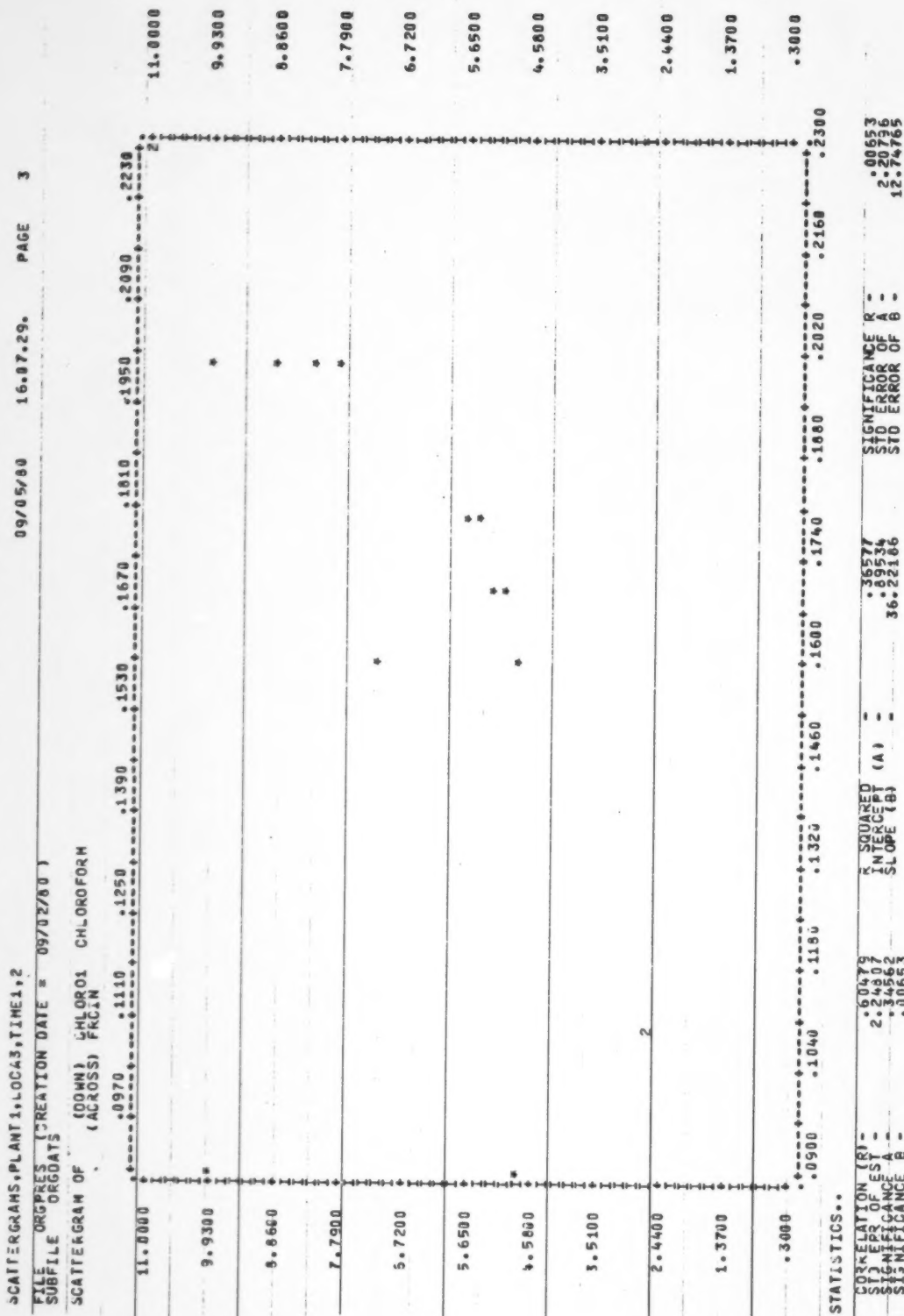


FIGURE 6. SCATTERGRAM OF CHLOROFORM VERSUS FREE CHLORINE RESIDUAL .



***** IS PRINTED IF A COEFFICIENT CANNOT BE COMPUTED.

FIGURE 7. SCATTERGRAM OF CHLOROFORM VERSUS NITROGEN SPECIES

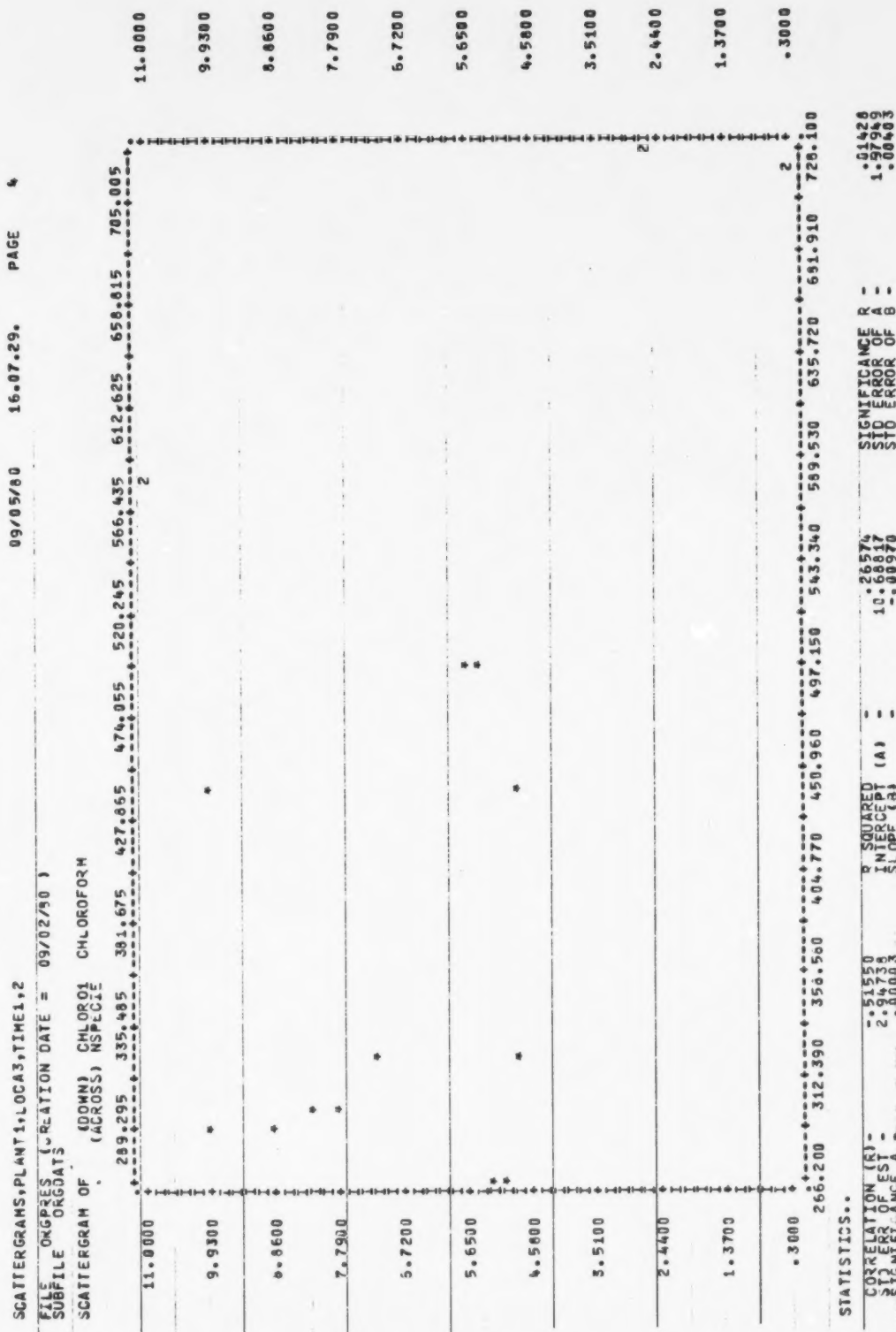


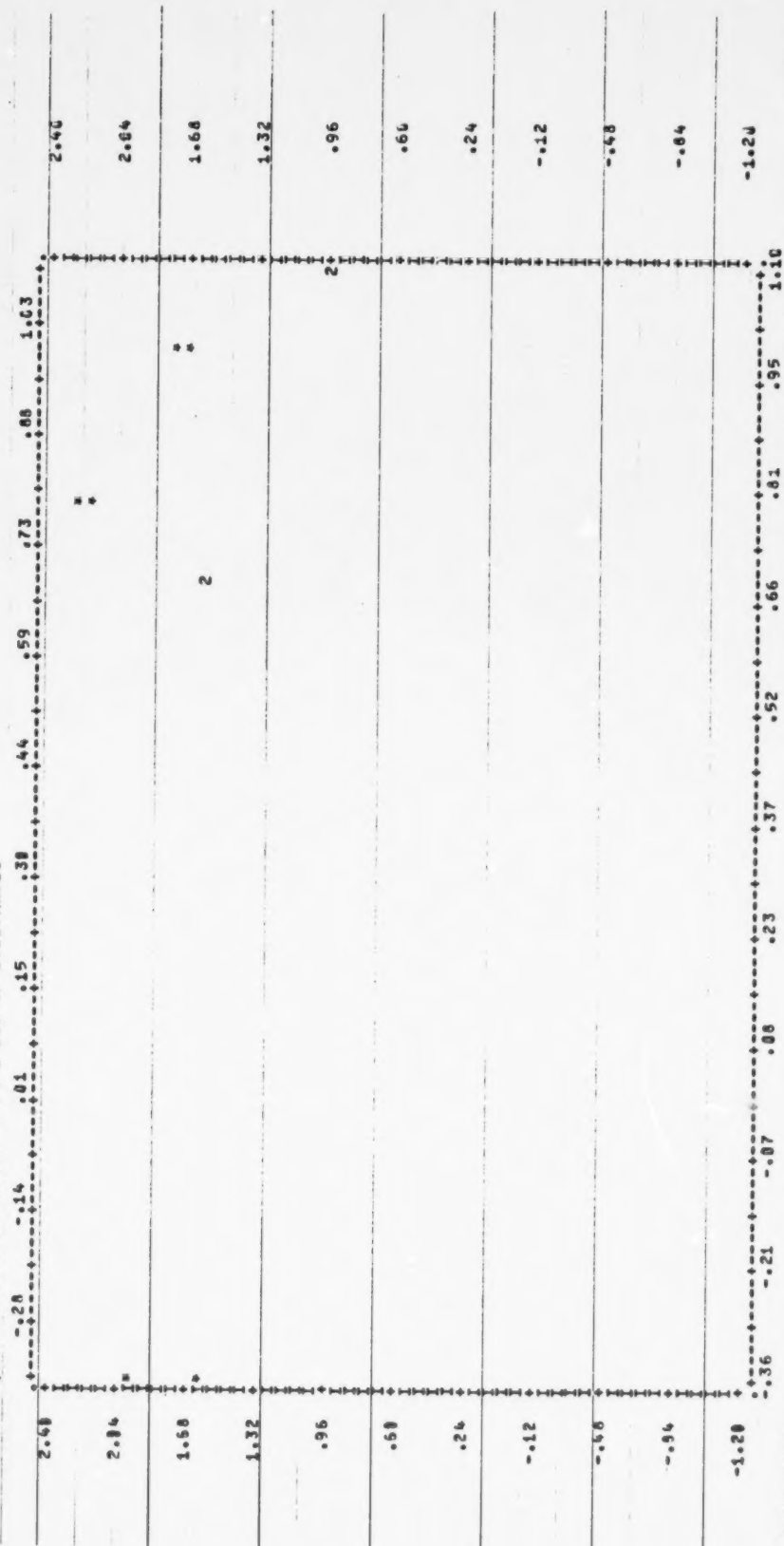
FIGURE 8. SCATTERGRAM OF LOG CHLOROFORM VERSUS LOG SUBSTRATE

SCATTERGRAMS, PLANT1, LOCAS, TIME1.2

FILE ORGPRES (CREATION DATE = 09/02/80)

09/05/80 16.17.05. PAGE 3

SCATTERGRAM OF (DOWN) LOGCHLOR NATURAL LOG OF CHLOROFORM
(ACROSS) LOGSUBST NATURAL LOG OF SUBSTRATES



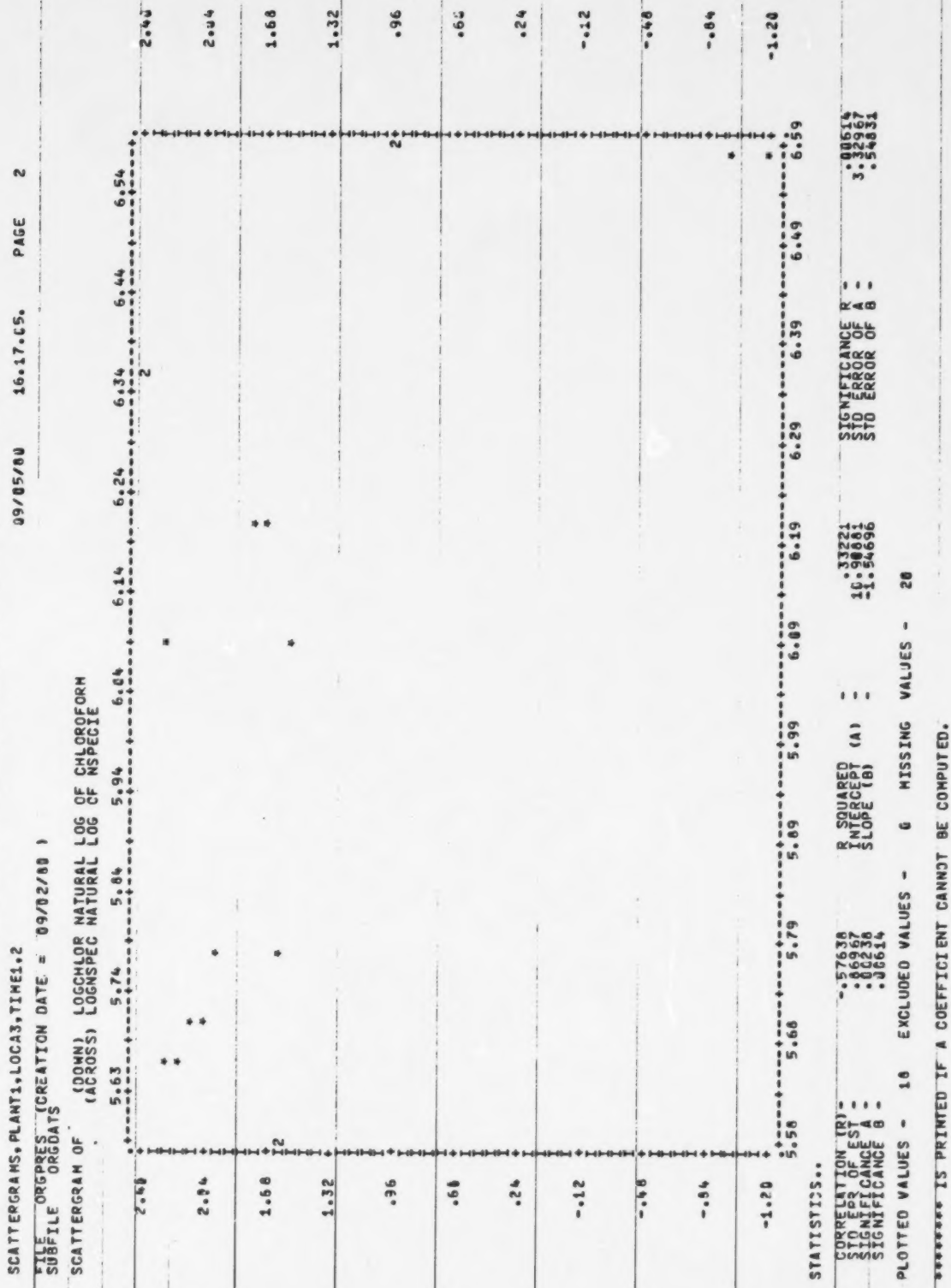
STATISTICS..

CORRELATION (R) = .9186
COEFFICIENT OF DETERMINATION (R²) = .8438
INTERCEPT (A) = 1.8392
SLOPE (B) = -.2405
SIGNIFICANCE A = .00002
SIGNIFICANCE B = .19728
PLOTTED VALUES - 10 EXCLUDED VALUES - 0 MISSING VALUES - 20

SIGNIFICANCE R = .19728
STD ERROR OF A = .22079
STD ERROR OF B = .26662

***** IS PRINTED IF A COEFFICIENT CANNOT BE COMPUTED.

FIGURE 9. SCATTERGRAM OF LOG CHLOROFORM VERSUS LOG NITROGEN SPECIES



Least-squares linear regressions of chloroform versus a precursor variable were run in conjunction with the scattergrams, .

The regression fit of chloroform concentration versus chlorine dose resulted in the following relationship:

$$\begin{array}{l} \text{Chloroform} \\ \text{Concentration} \end{array} (\mu\text{g/l}) = 4.36 [\text{chlorine dosage (mg/l)}] + 1.58 .$$

The standard error of prediction for the regression was 2.20 $\mu\text{g/l}$ with 39.5 percent of the variance in the chloroform concentrations explained by chlorine dosage. While this is a substantial percentage, it indicates that other variables singly and in conjunction are responsible for the majority of variance or that there is considerable random variability. Since the partial correlations showed that nitrogen species, bromide, and substrate were also involved, the results of the simple regression analysis are not surprising.

The regression equation also implies that the background chloroform concentration (that is, in the absence of chlorination) would be 1.58 $\mu\text{g/l}$. This is higher than the actual value of 0.53 $\mu\text{g/l}$ and may stem from the fact that the significance level of the intercept is relatively low ($P = 0.20$) and from the large standard error (35.2 percent relative to the mean chloroform concentration of 6.23 $\mu\text{g/l}$). It may also indicate that a linear model does not extrapolate to background conditions.

The results also suggest that the change in chloroform concentration at the outlet is 0.00436 times the change in chlorine dosage when both are in equivalent weight units. On a molar basis the relationship suggests that the change in chloroform concentrations (μM) is 0.0118 times the chlorine dosage in $\mu\text{moles per liter as HOC1}$.

For free residual chlorine the regression equation was:

$$\begin{array}{l} \text{Chloroform} \\ \text{Concentration} \end{array} (\mu\text{g/l}) = 36.22 [\text{Free Residual Chlorine (mg/l)}] + 0.895 .$$

The standard error of prediction for the regression was 2.25 $\mu\text{g/l}$ with 36.6 percent of the variance in chloroform concentration explained. The other variables appear to still require inclusion in a predictive equation since a majority of the variance is unexplained, or else considerable random variability is present.

The predicted background chloroform concentration of 0.895 $\mu\text{g/l}$ is closer to the actual value; however, the significance level of the value of the intercept is low ($P = 0.35$) and the relative standard error is still high (36.1 percent).

When the statistical outlier point was rejected as being greater than two standard errors from the least square line, the following regression was obtained:

$$\text{Chloroform Concentration } (\mu\text{g/l}) = 55.79 [\text{Free Residual Chlorine (mg/l)}] - 2.87 .$$

Again, the estimated background concentration is incorrect, however, the fit to the straight line is very good ($r = 0.869$). This relationship also explains the majority of variance in the chloroform concentrations (75.6 percent) and implies that free residual chlorine at the inlet may be a better predictor variable than chlorine dose. In addition, the free residual chlorine exhibited fewer confounding effects in the partial correlations, indicating that the prediction is less influenced by other variables.

The regressions of nitrogen species versus chloroform showed more scatter than the other regressions ($r = -.516$) and nitrogen species did not explain as large a portion of the variance as the chlorine precursors. The resulting regression fit was:

$$\text{Chloroform Concentration } (\mu\text{g/l}) = -0.0097 \left[\begin{array}{l} \text{Nitrogen} \\ \text{Species} \\ \text{Concentration} \end{array} (\mu\text{g/l}) \right] + 10.69 .$$

The standard error of prediction for the regression was 2.95 $\mu\text{g/l}$ with 26.6 percent of the variance explained.

Regression on the log-log plots produced the relationship:

$$\text{Log}_e \text{ Chloroform Concentration} = 1.55 \text{ Log}_e \left[\begin{array}{l} \text{Nitrogen} \\ \text{Species} \\ \text{Concentration} \end{array} (\mu\text{g/l}) \right] + 10.91 .$$

This equation predicted with a standard error of 0.870 log concentration units and explained 33.2 percent of the variance in the chloroform concentrations.

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APPENDIX A

DATA FOR VOLATILE AND SEMIVOLATILE
HALOGENATED ORGANICS FOR ALL PLANTS

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Allen 6/5/79																					
Lab Blank	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.4	"	"	"	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Intake	2.9	"	"	"	"	"	"	"	"	"	"	"	"	2.0	"	"	"	"	"	"	"
Inlet	7.8	"	"	"	"	"	"	"	"	"	"	"	"	2.0	"	"	"	"	"	"	"
Outlet-1	4.9	"	"	"	"	"	"	"	"	"	"	"	"	1.8	"	"	"	"	"	"	"
Outlet-2	10.0	"	"	"	"	"	"	"	"	"	"	"	"	1.9	"	"	"	"	"	"	"
Outlet-3	4.4	"	"	"	"	"	"	"	"	"	"	"	"	2.0	"	"	"	"	"	"	"
Intake	0.3	"	"	"	"	"	"	"	"	"	"	"	"	1.9	"	"	"	"	"	"	"
Allen 6/19/79																					
Lab Blank	0.4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.7	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.4	"	"	"	"	"	"	"
Intake	0.5	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	1.1	"	"	"	"	"	"	"
Inlet	8.0	"	"	0.8	<0.05	"	"	"	"	"	"	"	"	1.0	"	"	"	"	"	"	"
Outlet-1	8.3	"	"	1.0	0.1	"	"	"	"	"	"	"	"	0.9	"	"	"	"	"	"	"
Outlet-2	7.8	"	"	0.8	<0.05	"	"	"	"	"	"	"	"	0.9	"	"	"	"	"	"	"
Outlet-3	0.6	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.8	"	"	"	"	"	"	"
Intake	0.3	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	1.1	"	"	"	"	"	"	"

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by IVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Allen 7/10/79																					
Lab Blank	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.7	"	"	<0.05	<0.05	<0.05	"	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Intake	0.5	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Inlet	9.9	"	"	2.1	0.4	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-1	11.0	"	"	3.0	0.6	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-2	11.0	"	"	3.1	0.6	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-3	0.5	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Allen 8/7/79																					
Lab Blank	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.2	"	"	"	"	"	"	"	"	"	"	<0.05	"	0.4	"	"	"	"	"	"	"
Intake	0.5	"	"	"	"	"	"	"	"	"	"	0.2	"	1.6	"	"	"	"	"	"	"
Inlet	0.4	"	"	"	"	"	"	"	"	"	"	0.2	"	3.2	"	"	"	"	"	"	"
Outlet-1	0.4	"	"	"	"	"	"	"	"	"	"	0.1	"	0.8	"	"	"	"	"	"	"
Outlet-2	0.3	"	"	"	"	"	"	"	"	"	"	0.1	"	3.0	"	"	"	"	"	"	"
Outlet-3	0.3	"	"	"	"	"	"	"	"	"	"	0.1	"	1.8	"	"	"	"	"	"	"
Intake	0.2	"	"	"	"	"	"	"	"	"	"	0.1	"	1.9	"	"	"	"	"	"	"

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Allen 8/21/79																					
Lab Blank	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	<0.05	"	0.3	"	"	"	"	"	"	"
Inlet	0.05	"	"	<0.05	<0.05	"	"	"	"	"	"	<0.09	"	0.4	"	"	"	"	"	"	"
Outlet-1	3.1	"	"	0.7	<0.05	"	"	"	"	"	"	0.3	"	1.0	"	"	"	"	"	"	"
Outlet-2	5.0	"	"	0.9	<0.05	"	"	"	"	"	"	<0.05	"	1.0	"	"	"	"	"	"	"
Outlet-3	7.2	"	"	1.0	0.2	"	"	"	"	"	"	<0.05	"	0.4	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	<0.05	"	"	"	"	"	"	0.1	"	0.8	"	"	"	"	"	"	"
	0.3	"	"	<0.05	<0.05	"	"	"	"	"	"	0.2	"	0.1	"	"	"	"	"	"	"
Allen 9/25/79																					
Lab Blank	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	<0.05	"	0.5	"	"	"	"	"	"	"
Inlet	0.08	"	"	<0.05	<0.05	"	"	"	"	"	"	0.08	"	1.0	"	"	"	"	"	"	"
Outlet-1	10.0	"	"	1.1	0.3	"	"	"	"	"	"	<0.05	"	1.1	"	"	"	"	"	"	"
Outlet-2	9.0	"	"	1.0	0.2	"	"	"	"	"	"	<0.05	"	1.7	"	"	"	"	"	"	"
Outlet-3	10.0	"	"	1.8	0.3	"	"	"	"	"	"	<0.05	"	1.0	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	<0.05	"	"	"	"	"	"	<0.05	"	1.3	"	"	"	"	"	"	"
	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	0.06	"	1.0	"	"	"	"	"	"	"

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Alien 10/16/79																					
Lab Blank	0.06	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.16	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Inlet	0.08	<0.05	<0.05	0.3	0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.1	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05
Outlet-1	4.8	"	"	1.1	1.0	"	"	"	"	"	"	"	0.1	0.9	"	"	"	<0.05	"	"	"
Outlet-2	5.3	"	"	1.3	0.9	"	"	"	"	"	"	"	0.1	0.9	"	"	"	<0.05	"	"	"
Outlet-3	5.2	"	"	1.4	1.0	"	"	"	"	"	"	"	0.1	0.7	"	"	"	<0.05	"	"	"
Intake	0.3	"	"	0.9	0.8	"	"	"	"	"	"	"	<0.05	1.6	"	"	"	<0.05	"	"	"
	0.4	"	"	<0.05	0.6	"	"	"	"	"	"	"	<0.05	1.0	"	"	"	0.09	"	"	"
Allen 11/27/79																					
Lab Blank	0.1	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.2	"	"	<0.05	0.4	"	"	"	"	"	"	<0.05	"	0.2	"	<0.05	<0.05	"	"	"	"
Inlet	0.1	"	"	<0.05	1.0	"	"	"	"	"	"	0.07	"	1.0	"	0.6	0.06	"	"	"	"
Outlet-1	2.5	"	"	0.9	1.5	"	"	"	"	"	"	0.2	"	1.5	"	0.7	<0.05	"	"	"	"
Outlet-2	2.7	"	"	0.9	1.5	"	"	"	"	"	"	<0.05	"	1.4	"	0.7	<0.05	"	"	"	"
Outlet-3	2.7	"	"	0.4	1.0	"	"	"	"	"	"	0.2	"	1.2	"	0.7	<0.05	"	"	"	"
Intake	0.2	"	"	<0.05	1.0	"	"	"	"	"	"	<0.05	"	1.8	"	0.7	<0.05	"	"	"	"
	0.08	"	"	<0.05	0.9	"	"	"	"	"	"	0.07	"	1.4	"	0.6	0.06	"	"	"	"

*Sample broken in transit.

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Allen 12/11/79																					
Lab Blank	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2†	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	<0.05	"	"	<0.05	"	"	"	"	"	"	"	0.2†	<0.05	<0.05	"	"	"	"	"	"	"
Intake	0.08	"	"	<0.05	"	"	"	"	"	"	"	0.2†	0.08	0.7	"	"	"	"	"	"	"
Inlet	5.2	"	"	0.4	"	"	"	"	"	"	"	0.2†	0.06	0.5	"	"	"	"	"	"	"
Outlet-1	5.8	"	"	0.5	"	"	"	"	"	"	"	0.2†	0.1	0.4	"	"	"	"	"	"	"
Outlet-2	5.5	"	"	0.5	"	"	"	"	"	"	"	0.2†	0.1	0.4	"	"	"	"	"	"	"
Outlet-3	0.2	"	"	<0.05	"	"	"	"	"	"	"	0.2†	0.08	0.5	"	"	"	"	"	"	"
Intake	0.1	"	"	<0.05	"	"	"	"	"	"	"	0.2†	0.06	0.2	"	"	"	"	"	"	"
Kingston 6/26/79																					
Lab Blank	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	"	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.3	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	0.3	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Inlet	3.4	"	"	0.3	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-1	4.8	"	"	0.7	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-2	4.4	"	"	0.7	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-3	0.2	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	0.3	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"

†Probable contamination

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Kingston 7/10/79																					
Lab Blank																					
Trip Blank	0.04	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Intake	0.2	"	"	<0.05	"	"	"	"	"	"	"	"	"	1.4†	"	"	"	"	"	"	"
Inlet	3.2	"	"	0.4	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Outlet-1	3.0	"	"	0.6	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Outlet-2	4.3	"	"	0.5	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Outlet-3	0.4	"	"	<0.05	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	"	"	"	"	"	"	"	"	"	<0.05	"	"	"	"	"	"	"
Kingston 8/7/79																					
Lab Blank																					
Trip Blank	0.08	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Intake	0.2	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.2	"	"	"	"	"	"	"
Inlet	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.2	"	"	"	"	"	"	"
Outlet-1	4.4	"	"	0.4	<0.05	"	"	"	"	"	"	"	"	0.5	"	"	"	"	"	"	"
Outlet-2	7.2	"	"	1.0	0.9	"	"	"	"	"	"	"	"	0.5	"	"	"	"	"	"	"
Outlet-3	5.4	"	"	1.0	0.09	"	"	"	"	"	"	"	"	0.6	"	"	"	"	"	"	"
Intake	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.8	"	"	"	"	"	"	"
	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	0.2	"	"	"	"	"	"	"

†Probable contamination

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Kingston 8/21/79																					
Lab Blank	1.8†	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Intake	0.07	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Inlet	2.1	"	"	0.3	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-1	4.3	"	"	0.7	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-2	3.6	"	"	0.6	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-3	0.1	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	0.1	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Kingston 9/11/79																					
Lab Blank	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	<0.05	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Inlet	3.0	"	"	0.3	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-1	6.0	"	"	0.9	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-2	4.8	"	"	0.7	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Outlet-3	<0.05	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
Intake	<0.05	"	"	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"

*Sample broken in transit

†Probable contamination

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Kingston 10/10/79																					
Lab Blank	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.2	"	"	<0.05	"	"	"	"	"	"	"	"	"	0.4	"	"	"	"	"	"	"
Intake	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Inlet	6.3	<0.05	<0.05	0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Outlet-1	4.0	"	"	0.4	"	"	"	"	"	"	"	"	"	0.6	"	"	"	"	"	"	"
Outlet-2	5.0	"	"	0.8	"	"	"	"	"	"	"	"	"	0.4	"	"	"	"	"	"	"
Outlet-3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Intake	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Kingston 11/14/79																					
Lab Blank	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.2	<0.05	"	<0.05	"	"	"	"	"	"	"	"	"	0.3	"	"	"	"	"	"	"
Intake	0.2	<0.05	"	<0.05	"	"	"	"	"	"	"	"	"	0.2	"	"	"	"	"	"	"
Inlet	4.4	0.2	"	0.5	"	"	"	"	"	"	"	"	"	0.4	"	"	"	"	"	"	"
Outlet-1	4.0	0.2	"	0.4	"	"	"	"	"	"	"	"	"	0.3	"	"	"	"	"	"	"
Outlet-2	3.6	0.2	"	0.6	"	"	"	"	"	"	"	"	"	0.3	"	"	"	"	"	"	"
Outlet-3	0.2	<0.05	"	<0.05	"	"	"	"	"	"	"	"	"	0.2	"	"	"	"	"	"	"
Intake	0.08	<0.05	"	<0.05	"	"	"	"	"	"	"	"	"	0.06	"	"	"	"	"	"	"

*Sample broken in transit

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Kingston 12/18/79																					
Lab Blank	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	<0.05	"	"	"	<0.05	"	"	"	0.07	0.3	"	"	"	"	"	"	"
Inlet	0.08	"	"	<0.05	<0.05	"	"	"	1.1	"	"	"	0.1	0.1	"	"	"	"	"	"	"
Outlet-1	3.8	"	"	0.5	0.08	"	"	"	60.0	"	"	"	0.05	0.3	"	"	"	"	"	"	"
Outlet-2	4.8	"	"	0.6	0.08	"	"	"	16.0	"	"	"	0.1	0.2	"	"	"	"	"	"	"
Outlet-3	4.5	"	"	0.7	0.08	"	"	"	5.0	"	"	"	0.06	0.2	"	"	"	"	"	"	"
Intake	0.1	"	"	<0.05	<0.05	"	"	"	30.0	"	"	"	0.06	0.1	"	"	"	"	"	"	"
	0.1	"	"	<0.05	<0.05	"	"	"	0.08	"	"	"	<0.05	0.2	"	"	"	"	"	"	"
Shawnee 6/12/79																					
Lab Blank	0.4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Inlet	0.9	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Outlet-1	10.0	<0.05	<0.05	2.2	0.4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Outlet-2	10.0	"	"	2.2	0.4	"	"	"	"	"	"	"	2.7	3.5	"	"	"	"	"	"	"
Outlet-3	0.6	"	"	<0.05	<0.05	"	"	"	"	"	"	"	3.9	3.7	"	"	"	"	"	"	"
Intake	0.4	"	"	<0.05	<0.05	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"

*Sample broken in transit

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Shawnee 6/26/79																					
Lab Blank	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Intake	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Inlet	9.5	"	"	1.1	0.2	"	"	"	"	"	"	6.0	"	"	"	"	"	"	"	"	"
Outlet-1	9.6	"	"	1.2	0.2	"	"	"	"	"	"	9.0	"	"	"	"	"	"	"	"	"
Outlet-2	9.7	"	"	1.4	0.2	"	"	"	"	"	"	8.4	"	"	"	"	"	"	"	"	"
Outlet-3	0.5	"	"	<0.05	<0.05	"	"	"	"	"	"	7.8	"	"	"	"	"	"	"	"	"
Intake	0.3	"	"	<0.05	<0.05	"	"	"	"	"	"	8.2	"	"	"	"	"	"	"	"	"
Shawnee 7/24/79																					
Lab Blank	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	"	"	"	"	"	"	"	0.08	"	"	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	"	"	"	"	"	"	"	7.5	"	"	"	"	"	"	"	"	"
Inlet	6.0	"	"	0.1	"	"	"	"	"	"	"	8.8	"	"	"	"	"	"	"	"	"
Outlet-1	18.0	"	"	0.8	"	"	"	"	"	"	"	13.0	"	"	"	"	"	"	"	"	"
Outlet-2	18.0	"	"	0.6	"	"	"	"	"	"	"	13.0	"	"	"	"	"	"	"	"	"
Outlet-3	0.2	"	"	<0.05	"	"	"	"	"	"	"	7.6	"	"	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	"	"	"	"	"	"	"	6.5	"	"	"	"	"	"	"	"	"

*Sample broken in transit

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobutane	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene
Shawnee 8/14/79																					
Lab Blank	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.2	<0.05	"	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.1	"	"	<0.05	<0.05	"	"	"	"	"	"	<0.05	"	5.5	"	"	"	"	"	"	"
Intake	0.2	"	"	<0.05	0.08	"	"	"	"	"	"	6.0	"	3.0	"	"	"	"	"	"	"
Inlet	5.0	"	"	0.4	0.1	"	"	"	"	"	"	5.1	"	3.4	"	"	"	"	"	"	"
Outlet-1	5.0	"	"	0.4	<0.05	"	"	"	"	"	"	4.6	"	3.6	"	"	"	"	"	"	"
Outlet-2	5.0	"	"	0.4	<0.05	"	"	"	"	"	"	5.0	"	3.0	"	"	"	"	"	"	"
Outlet-3	0.2	"	"	<0.05	<0.05	"	"	"	"	"	"	4.4	"	4.2	"	"	"	"	"	"	"
Intake	0.08	"	"	<0.05	0.06	"	"	"	"	"	"	2.4	"	0.4	"	"	"	"	"	"	"
Shawnee 10/2/79																					
Lab Blank	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trip Blank	0.3	"	<0.05	<0.05	<0.05	"	"	"	"	"	"	<0.05	0.4	0.3	"	"	"	"	"	"	"
Intake	0.2	"	0.4	<0.05	0.1	"	"	"	"	"	"	2.6	<0.05	0.2	"	"	"	"	"	"	"
Inlet	13.6	"	0.3	1.8	0.4	"	"	"	"	"	"	4.6	0.2	0.3	"	"	"	"	"	"	"
Outlet-1	12.0	"	0.4	1.7	0.4	"	"	"	"	"	"	4.2	<0.05	0.2	"	"	"	"	"	"	"
Outlet-2	8.0	"	0.6	1.2	0.3	"	"	"	"	"	"	4.4	0.2	0.2	"	"	"	"	"	"	"
Outlet-3	0.6	"	0.3	<0.05	0.3	"	"	"	"	"	"	4.6	0.1	0.2	"	"	"	"	"	"	"
Intake	0.5	"	0.4	<0.05	0.2	"	"	"	"	"	"	3.8	0.07	0.08	"	"	"	"	"	"	"

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES (µg/l) (Continued)
Performed by TVA Laboratory Branch

Shawnee 11/6/79	Chloroform	Bromoform	Bromochloromethane	Bromodichloromethane	Dibromochloromethane	Trichlorofluoromethane	Methyl Bromide	Methyl Chloride	Methylene Chloride	Chloroethane	1,1-Dichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,1,1-Trichloroethane	Chlorobenzene	1,4-Dichlorobenzene	trans-1,2-Dichloroethylene	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane	1,2-Dichloropropane	1,1-Dichloroethylene	
	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	
Lab Blank	0.08	"	<0.05	<0.05	<0.05	"	"	"	"	"	<0.05	<0.05	<0.05	0.1	"	"	"	"	"	"	<0.05	
Trip Blank	0.5	"	5.0	<0.05	0.2	"	"	"	"	"	0.1	4.1	0.2	0.1	"	"	"	"	"	"	<0.05	
Intake	0.5	"	5.0	<0.05	0.2	"	"	"	"	"	<0.05	5.9	0.2	0.2	"	"	"	"	"	"	0.5	
Inlet	5.2	"	3.9	0.8	0.3	"	"	"	"	"	<0.05	5.2	<0.05	<0.05	"	"	"	"	"	"	0.4	
Outlet-1	4.8	"	1.0	0.5	0.2	"	"	"	"	"	<0.05	5.2	<0.05	<0.05	"	"	"	"	"	"	<0.05	
Outlet-2	4.6	"	5.6	0.6	0.2	"	"	"	"	"	<0.05	5.4	0.1	<0.05	"	"	"	"	"	"	0.2	
Outlet-3	0.5	"	2.5	<0.05	0.1	"	"	"	"	"	<0.05	3.7	0.09	0.2	"	"	"	"	"	"	0.2	
Intake	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

*Sample broken in transit

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES* (µg/l)

	Methyl Chloride	Dichlorofluoromethane	Methyl Bromide	Chloroethane	Trichlorofluoromethane	1,1-Dichloroethylene	Methylene Chloride	trans-1,2-Dichloroethylene	1,1-Dichloroethane	Chloroform	1,1,1-Trichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,2-Dichloropropane	1,3-Dichloropropane	Bromodichloromethane	1,1,2-Trichloroethane	Dibromochloromethane	Chlorobenzene	Bromoform	1,1,2,2-Tetrachloroethane
Kingston 9/11/79																					
Trip Blank	4	19	<10	<10	1.4	0.8	35.0	<0.1	0.1	7.0	5.7	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<1.0	<1.0
Inlet-1	6	15	<10	<10	0.4	0.2	11.9	<0.1	0.1	13.3	2.1	0.3	<0.1	<0.1	<0.1	0.9	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-2	7	12	<10	<10	1.1	0.1	13.4	<0.1	0.1	17.5	0.9	0.2	<0.1	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	6	17	<10	<10	3.0	0.6	12.7	<0.1	0.1	15.6	1.9	0.2	0.1	<0.1	<0.1	1.1	<0.1	<0.1	<0.1	<1.0	<1.0
Allen 9/25/79																					
Trip Blank	11	21	<10	<10	4.0	15.3	31.1	0.1	0.1	5.7	2.8	0.4	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Inlet-1	6	19	<10	<10	1.7	15.4	20.7	0.1	0.2	31.0	3.5	0.4	0.1	0.1	0.1	3.2	0.1	0.1	0.1	0.1	0.1
Outlet-2	6	17	<10	<10	1.5	1.6	11.5	0.1	0.3	43.9	3.7	0.2	0.1	0.1	0.1	5.5	0.1	0.1	0.1	0.1	0.1
Outlet-3	10	10	<10	<10	2.0	1.9	5.8	0.1	0.2	26.2	3.8	1.1	0.6	0.1	0.1	2.9	0.1	0.1	0.1	0.1	0.1
Shawnee 10/2/79																					
Trip Blank	10	22	<10	<10	5.0	6.1	160	0.6	0.3	20.3	5.4	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1.0	1.0
Intake	8	14	<10	<10	16	1.9	12	0.1	0.4	1.8	0.7	7.8	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1.0	1.0
Inlet-1	12	18	<10	<10	12	6.0	15	0.1	0.7	20.1	0.4	11.7	0.2	0.1	0.1	0.6	0.1	0.1	0.1	1.0	1.0
Outlet-2	9	17	<10	<10	22	4.9	16	0.1	0.7	44.4	3.4	18.0	0.3	0.1	0.1	1.0	0.2	0.1	0.1	1.0	1.0
Outlet-3	7	29	<10	<10	23	3.0	17	0.1	0.6	45.0	4.4	17.0	0.3	0.1	0.1	1.0	0.2	0.1	0.1	1.0	1.0
Outlet-3 + 20 ppb	32	53	17	17	36	21	31	18.6	27.2	73.2	18.8	42.2	20.0	21.0	26.6	32.0	23.3	17.6	17.5	20.2	33.3
Shawnee 11/6/79																					
Trip Blank ^a	<50	<20	<50	<50	<1.0	<0.1	37.4	<0.1	<0.1	3.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Inlet-1	<50	<20	<50	<50	5.2	<0.1	1.5	<0.1	<0.1	3.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Outlet-2	<50	<20	<50	<50	4.2	<0.1	6.8	<0.1	<0.1	3.0	<0.1	4.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	1.5	<0.1	<0.1	0.9	<0.1	6.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	56.6	<1.1	<0.1	5.3	<0.1	5.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	0.1	<0.5	<0.1	11.1	<0.1	5.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	5.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0
Lab Blank	<50	<20	<50	<50	<1.0	<0.1	1.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0

^aWater supplied by TVA.

*Performed by Battelle-Columbus Laboratories; data not evaluated statistically.

SUMMARY OF VOLATILE HALOGENATED ORGANICS ANALYSES* (µg/l) (Continued)

	Methyl Chloride	Dichlorofluoromethane	Methyl Bromide	Chloroethane	Trichlorofluoromethane	1,1-Dichloroethylene	Methylene Chloride	trans-1,2-Dichloroethylene	1,1-Dichloroethane	Chloroform	1,1,1-Trichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	1,2-Dichloropropane	1,3-Dichloropropane	Bromodichloromethane	1,1,2-Trichloroethane	Dibromochloromethane	Chlorobenzene	Bromoform	1,1,2,2-Tetrachloroethane
Kingston 11/14/79																					
Trip Blank ^a	<50	<20	<50	<50	6.8	1.1	4.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Inlet-1	<50	<20	<50	<50	22.0	<0.1	2.5	<0.1	<0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-2	<50	<20	<50	<50	10.4	<0.1	5.4	<0.1	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	<1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	<1.0	<0.1	1.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	18.7	<0.1	1.8	<0.5	<0.1	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	16.6	<0.1	2.7	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Lab Blank	<50	<20	<50	<50	<1.0	<0.1	1.5	<0.1	<0.1	4.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Lab Blank	50	20	50	50	<1.0	0.2	2.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Allen 11/27/79																					
Trip Blank ^a	<50	<20	<50	<50	15.5	4.2	0.9	<0.1	<0.1	<0.1	<3.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Inlet-1	<50	<20	<50	<50	91.2	18.2	67.3	<0.1	<0.1	<0.1	<1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-2	<50	<20	<50	<50	1558.8	269.7	4.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	9.1	23.7	1.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	165.7	47.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	9.7	5.8	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-3	<50	<20	<50	<50	20.5 ^b	4.9	13.2	<0.1 ^b	<0.1	<0.1	0.8 ^b	<0.1 ^b	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0
Outlet-2 + 20 ppb	<50	13.6	<50	<50	63.0 ^b	46.6	57.2	73.6 ^b	20.2	20.3	101.9 ^b	68.8 ^b	22.3	<0.1	<0.1	56.1 ^b	8.0	11.4	11.7	48.3 ^b	42.3
Lab Blank	<50	<20	<50	<50	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<1.0

^aWater supplied by TVA.

^bThese analytes were spiked at 50 ppb.

*Performed by Battelle-Columbus Laboratories; data not evaluated statistically.

SUMMARY OF SEMIVOLATILE HALOGENATED ORGANICS ANALYSES* ($\mu\text{g/l}$)
 Performed by TVA Laboratory Branch

Plant	2-Chloronaphthalene	1,2-Dichlorobenzene	2-Chlorophenol
<u>Kingston (9/11/79)</u>			
Intake			
Inlet	<1.0	1.8	
Outlet	1.2	<1.0	
	1.0	<1.0	
<u>Allen (9/25/79)</u>			
Intake			
Inlet	<1.0		
Outlet	2.0		
	<1.0		
<u>Allen (11/27/79)</u>			
Intake			<10.0
Inlet			79.0
Outlet			<10.0

APPENDIX B

DATA FOR PRECURSORS, AMINO ACIDS,
AND WATER QUALITY FOR ALL PLANTS

SUMMARY OF PRECURSORS ANALYSES*

	Date	Br ⁻ (µg/l)	NH ₃ (µg/l)	Natural Color (mg Pt/l)	Polyhydroxy- benzenes (mg/l)	Humic acids (mg/l)	Fulvic acids (mg/l)
Kingston Kingston Blank	8-21	116 280	70.7 32.2	0.5 0.0	2.6 0.0	1.6 0.0	1.1 0.0
Allen Allen Blank	8-21	300 61.0	9.2 <8.5	insufficient sample	6.5 0.6	0.2 0.0	0.5 0.0
Kingston Kingston Blank	9-11	172 60.0	16.1 9.0	0.6 0.0	3.9 0.0	0.5 0.0	0.6 0.0
Allen Allen Blank	9-25	225 60.7	19.6 <8.5	3.2 0.0	5.0 0.0	1.5 0.0	0.7 0.0
Shawnee Shawnee Blank	10-2	168 63.0	23.0 <8.5	1.5 0.0	25.5 0.0	1.6 0.0	0.6 0.0
Kingston Kingston Blank	10-10	112 63.0	18.7 <8.5	0.8 0.0	2.3 0.0	1.5 0.0	0.4 0.0
Allen Allen Blank	10-16	670 62.2	19.6 <8.5	1.9 0.0	5.4 0.0	0.8 0.0	1.2 0.0
Shawnee Shawnee Blank	11-6	46.4 <40	<8.5 <8.5	0.7 0.0	2.4 0.0	1.0 0.0	0.5 0.0
Kingston Kingston Blank	11-14	<40 <40	8.2 <8.5	0.5 0.0	0.9 0.0	0.8 0.0	0.5 0.0
Allen Allen Blank	11-27	99.8 <40	159.8 <8.5	3.0 0.0	4.5 0.0	1.5 0.0	1.5 0.0
Kingston Kingston Blank	12-18	<40 <40	25.5 17.0	0.4 0.0	2.4 0.0	0.5 0.0	0.4 0.0
Allen Allen Blank	12-11	95.8 <40	204 <8.5	1.8 0.0	3.3 0.0	1.4 0.0	1.3 0.0

*Performed by Battelle-Columbus Laboratories.

SUMMARY OF AMINO ACID ANALYSES * (µg/l)

Sample	Aspartic Acid	Threonine	Serine	Glutamic acid	Proline	Glycine	Alanine	Cystine	Valine	Methionine	Isoleucine	Leucine	Tyrosine	Phenylalanine	Histidine	Lysine	Arginine	Tryptophan	Asparagine	Glutamine
Kingston	2.0	1.0	3.7	1.1	1.6	3.2	1.9	<0.5	1.7	<0.5	<0.5	0.7	1.2	<0.5	1.6	3.0	<0.5	-	-	-
Blank	1.1	0.7	3.0	0.6	<0.5	1.6	0.6	<0.5	0.6	<0.5	<0.5	<0.5	0.5	<0.5	0.5	1.9	<0.5	-	-	-
Allen	0.5	0.8	2.2	<0.5	0.8	1.3	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	0.8	2.8	<0.5	-	-	-
Blank																				
Kingston	9/11/79 Not Analyzed Due to Breakage in Transit.																			
Blank																				
Allen	0.8	0.5	1.4	1.1	<0.5	0.9	0.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	2.2	<0.5	-	-	-
Blank	<0.5	<0.5	1.2	<0.5	<0.5	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	-	-	-
Shawnee	2.2	1.6	7.2	1.8	0.6	3.4	2.1	<0.5	1.4	<0.5	0.6	1.0	0.9	1.1	2.2	5.7	<0.5	-	-	-
Blank	0.8	<0.5	1.7	<0.5	<0.5	0.9	1.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	-	-	-
Kingston	<0.5	<0.5	1.6	<0.5	<0.5	0.9	<0.5	<0.5	<0.5	<2.0	<0.5	<0.5	<0.5	<0.5	0.6	0.6	<0.5	<0.5	1.2	2.3
Blank	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-	-	-
Allen	<0.5	<0.5	1.1	<0.5	<0.7	0.6	<0.5	<0.5	<0.5	<2.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.6	<0.5	<0.5	2.0	1.8
Shawnee	0.5	<0.5	1.3	0.5	<0.5	0.8	<0.5	<0.5	<0.5	<2.0	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	2.0	1.7
Kingston	1.3	2.7	13.4	0.7	2.1	6.0	3.5	<0.5	2.1	<2.0	1.1	1.4	1.4	1.1	3.1	6.6	<0.5	<0.5	1.5	8.3
Allen	0.6	<0.5	1.2	0.8	<0.5	0.7	<0.5	<0.5	<0.5	<2.0	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	2.2	1.8
Kingston	2.8	1.8	9.2	1.3	0.9	4.4	2.5	<0.5	0.9	<2.0	0.7	1.0	0.8	1.0	1.7	5.7	<0.5	<0.5	1.1	6.8
Allen	0.6	<0.5	1.2	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	1.2	0.6
Blank	2.5	0.9	1.8	2.5	0.9	1.3	1.9	<0.5	0.6	1.4	0.7	0.6	<0.5	<0.5	0.6	1.2	<0.5	<0.5	1.2	0.6

*Performed by Battelle-Columbus Laboratories.

SUMMARY WATER QUALITY DATA
Performed by TVA Laboratory Branch

Plant	Date	Organic Nitrogen mg/l	NH ₃ mg/l	NO ₂ /NO ₃ mg/l ³	TOC mg/l	Total Alkalinity mg/l	TSS mg/l	Specific Conductivity mmho	Total Fe µg/l	Ca mg/l	Mg mg/l	Hardness mg/l	pH
Allen	6/5/79	0.34	0.10	1.0	7.1	55	99	156	1400	11	5.7	-	7.3
	6/19/79	0.17	0.13	1.4	6.0	70	30	240	900	19	8.2	81	7.3
	7/10/79	0.26	0.32	1.4	8.6	98	15	340	1500	39	13.0	150	7.5
	8/7/79	0.70	0.02	1.4	5.4	100	14	360	1100	36	12.0	140	7.4
	8/21/79	0.27	0.04	-	5.2	110	14	340	660	35	11.0	13	7.7
	9/25/79	0.26	0.02	1.4	6.6	97	11	320	1800	35	13.0	-	-
	10/16/79	0.21	0.05	1.4	5.2	96	11	310	1100	30	12.0	-	7.3
	11/27/79	0.40	0.32	0.85	6.6	74	29	340	1000	35	7.9	93	7.3
	12/11/79	0.34	0.15	0.94	5.0	78	10	240	1700	31	8.4	110	7.1
Kingston	6/26/79	0.23	0.11	0.51	2.6	80	29	210	390	25	7.4	93	7.6
	7/10/79	0.10	0.06	0.42	2.2	59	25	170	600	22	5.8	74	7.2
	8/7/79	0.07	0.03	0.48	2.4	79	20	210	1800	26	5.7	88	7.3
	8/21/79	0.14	0.02	0.79	2.4	90	15	220	620	28	8.0	100	7.4
	9/11/79	0.12	0.02	0.43	2.9	96	13	240	480	32	8.9	116	8.0
	10/10/79	0.22	0.03	0.47	4.1	75	11	190	550	17	6.0	67	7.5
	11/14/79	0.10	0.01	0.19	2.2	-	-	45	700	6.7	1.8	24	7.0
	12/18/79	-	0.03	0.31	2.0	69	9	180	410	26	7.0	94	7.9
	6/12/79	0.12	0.06	0.67	4.0	83	26	180	1100	25	5.9	87	7.3
	6/26/79	0.14	0.06	0.37	3.6	51	80	160	1800	19	4.3	65	7.7
	7/24/79	0.16	0.04	0.15	4.3	51	34	140	650	16	3.3	54	7.4
	8/14/79	0.12	0.06	0.34	4.4	68	41	290	1700	22	6.0	80	7.3
Shawnee	10/2/79	0.18	0.01	0.44	5.8	56	39	150	690	21	4.5	71	7.4
	11/6/79	0.11	0.03	0.36	3.0	60	28	150	730	21	3.7	68	7.3

SUMMARY WATER QUALITY DATA (Continued)
Performed by TVA Laboratory Branch

Plant	Date	Chlorine Dosage Calculated mg/ℓ	Cooling Water Rate gpm	Free Residual Chlorine		Total Residual Chlorine		Temperature of	
				Inlet (a)	Outlet (a)	Inlet (a)	Outlet (a)	Intake	Outlet
Allen	6/5/79	0.97	102,897	0.09	0.11	0.16	0.22	70	70.0
	6/19/79	1.15	108,541	0.20	0.24	0.44	0.40	75.9	75.9
	7/10/79	2.10	108,941	0.23	0.12	0.50	0.40	78.8	79.3
	8/7/79	1.53	135,575	0.17	0.25	0.13	0.13	83.5	83.5
	8/21/79	1.53	135,575	0.16	0.12	0.32	0.29	82.2	82.2
	9/25/79	1.13	125,596	0.20	0.14	0.41	0.26	73.4	73.0
	10/16/79	1.04	112,446	0.17	0.13	0.31	0.22	51.8	65.4
	11/27/79	0.80	124,261	0.11	0.10	0.45	0.41	52	53.5
	12/11/79	1.15	86,673	0.18	0.12	0.65	0.59	46.4	46.5
Kingston	6/26/79	0.60	110,619	0.33	0.30	0.49	0.46	70	70
	7/10/79	0.60	110,619	0.06	0.13	0.35	0.38	69	70
	8/7/79	0.86	106,039	0.24	0.36	0.40	0.52	66	72
	8/21/79	0.86	106,039	0.21	0.22	0.32	0.36	68	71
	9/11/79	0.79	106,039	0.30	0.19	0.55	0.45	68	74
	10/10/79	1.13	103,364	0.58	0.46	0.66	0.69	64	68
	11/14/79	1.05	111,396	0.49	0.75	0.78	0.85	51	52
	12/18/79	1.11	104,634	1.12	0.70	1.61	0.88	46	47
Shawnee	6/12/79	0.95	125,659	0.51	0.35	0.63	0.58	71	72
	6/26/79	1.10	116,040	0.46	0.31	0.63	0.55	74	77
	7/24/79	0.85	88,135	0.29	0.20	0.36	0.33	81	85
	8/14/79	0.58	122,831	0.09	0.12	0.25	0.22	77	80
	10/2/79	0.75	110,584	0.33	0.27	0.59	0.47	66	73
	11/6/79	0.61	121,930	0.12	0.15	0.27	0.29	59	61

(a) Average measurement.

APPENDIX C
QUALITY ASSURANCE DATA

QUALITY ASSURANCE DATA

Careful quality assurance practices were followed in the conduct of the analyses. Replicates were used to determine precision and spikes were used to verify accuracy. Battelle-Columbus quality assurance for precursors data are presented in Vigon and Stanford (1980). TVA's quality assurance program for halogenated organics is discussed in this section.

Precision for the extraction of volatile organic analyses was monitored by analyzing a surrogate standard. A single surrogate, 1,4-dichlorobutane, was used from June 15 through September 15, 1979. Every tenth sample (or one sample in each batch of samples, if less than ten samples analyzed) was spiked in duplicate with the surrogate and analyzed. Warning and control limits for precision were generated by determining the standard deviation of the RSD's for the first seven sets of duplicate data. Accuracy was assessed by comparing percent bias values for the 1,4-dichlorobutane surrogate to a mean value which was obtained by the same day analysis of 20 aliquots of the 1,4-dichlorobutane solution. However, surrogate data generated from early August through September 15, 1979 are suspect because the 1,4-dichlorobutane surrogate likely vaporized from its deionized water matrix during this period of abnormally high temperature in the laboratory. Data for samples during this interval have been judged satisfactory because standards were prepared in a methanol matrix rather than an aqueous matrix and previously constructed calibrated curves checked within limits.

Two surrogate compounds, bromochloromethane and 1-chloro-2-bromopropane were used to monitor the precision and accuracy of volatile organic analyses completed after September 15, 1979. These two surrogates more closely approximated the volatility of components that were being detected in the aqueous samples. Warning and control limits for precision observations were generated by determining the standard deviation of the relative standard deviations on ten sets of duplicate analyses done on November 9, 1979. Accuracy was assessed by comparing the percent bias values for the two surrogates to a mean percent bias value determined by the replicate analyses on the November 19, 1979 date.

Accuracy of volatile organic analyses was also assessed by analyzing EPA reference samples. EPA sample No. WS 1276--a set of two samples of different concentrations--was submitted and analyzed as an unknown on June 7, 1979, and November 9, 1979. Each analysis was done by a different analyst.

Semivolatile chlorinated organic analyses were monitored by duplicate spiking of every tenth sample with a representative compound from both the acid extractable and base-neutral fractions. Precision and accuracy of the acid extractable analyses were assessed by spiking the sample with 2,4-dichlorophenol. Warning and control limits for precision were generated by determining the standard deviation of the relative standard deviations for the first seven sets of duplicate data. Warning and control limits for accuracy were generated by determining the standard deviation of the percent bias values for the first seven pieces of 2,4-dichlorophenol-spiked data.

Precision and accuracy of the base-neutral analyses were assessed by spiking the sample with hexachlorobenzene. Warning and control limits for precision were generated by determining the standard deviation of the relative standard deviations for the first seven sets of duplicate data. Warning and control limits for accuracy were generated by determining the standard deviation of the percent bias values for the first seven sets of hexachlorobenzene-spiked data.

The quality assurance data for volatile organic analyses are shown graphically in Figures C-1 to C-3 and all data are tabulated in Table C-2 to C-13. Analysis of the EPA standards is shown in Table C-1.

One important factor which enters into the statistical analysis is that the analytical error of the dependent variable must be small relative to the range of that variable. If this is not the case then the significance of the statistical procedures is questionable. For the semivolatile compounds the analytical accuracy is within ± 10 percent. This is not expected to affect the statistical analyses for chloroform since the chloroform concentrations varied from 0.05 to 11.0 $\mu\text{g/l}$.

Finally, a set of tests were run to determine holding times for each of three analytes--chloroform, dichlorobromomethane, and chlorodibromomethane. At an average concentration of 23 $\mu\text{g/l}$ chloroform exhibited at 10 percent relative standard deviation. Dichlorobromomethane averaged 6.3 $\mu\text{g/l}$ and was the least variable at 4.2 percent relative standard deviation. Chlorodibromomethane was the most variable with an 11.3 percent relative standard deviation, but also had the lowest average concentration of 0.70 $\mu\text{g/l}$. None of the three compounds exhibited a tendency toward lower concentrations with time (Figure C-4). It was concluded that the volatile halogenated organics when properly stored could be kept for periods up to three weeks without degradation or volatility losses.

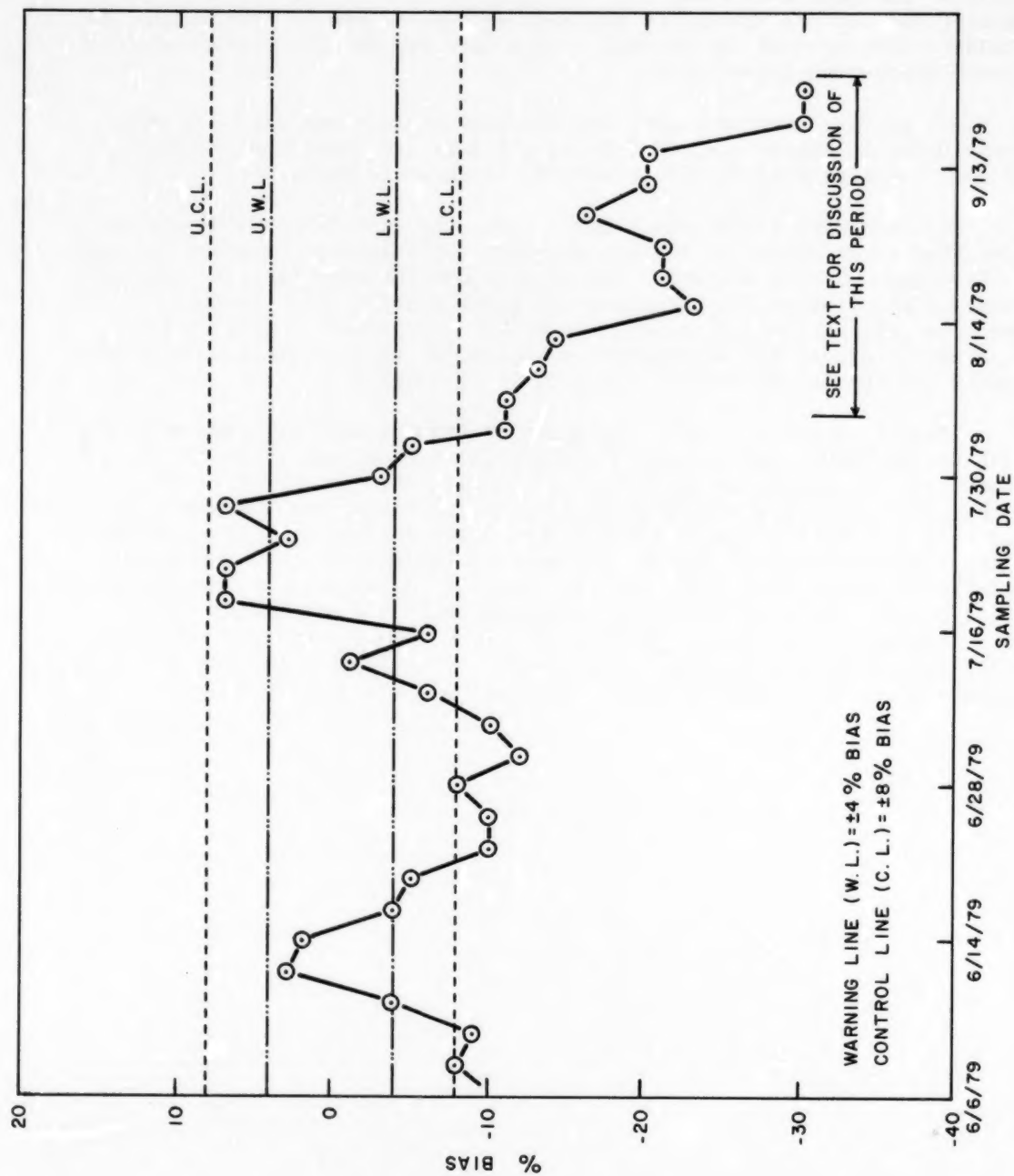


Figure C-1. Accuracy chart (1,4 dichlorobutane surrogate)
 for volatile halogenated organics

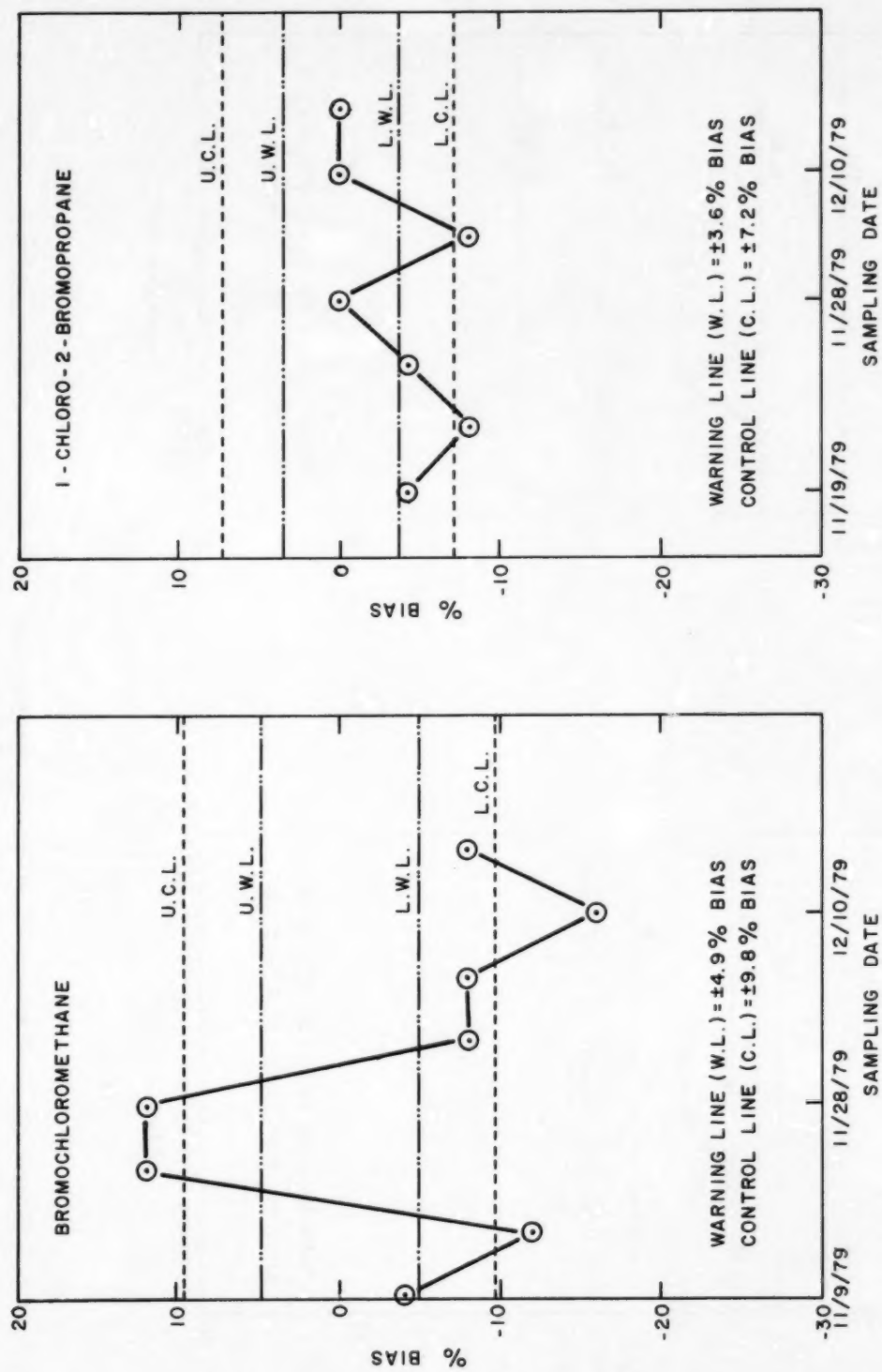


Figure C-2. Accuracy chart (bromochloromethane and 1-chloro-2-bromopropane) for volatile halogenated organics

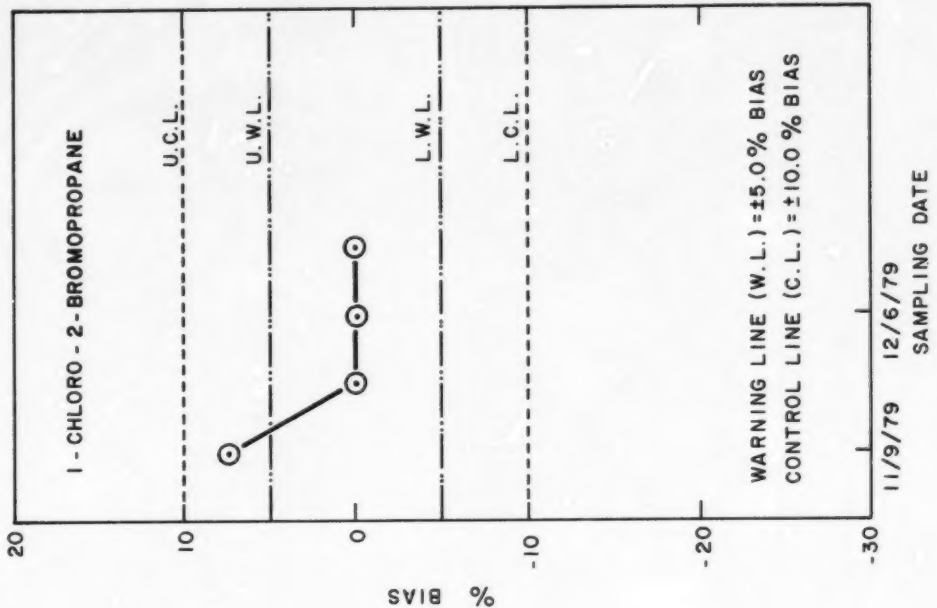
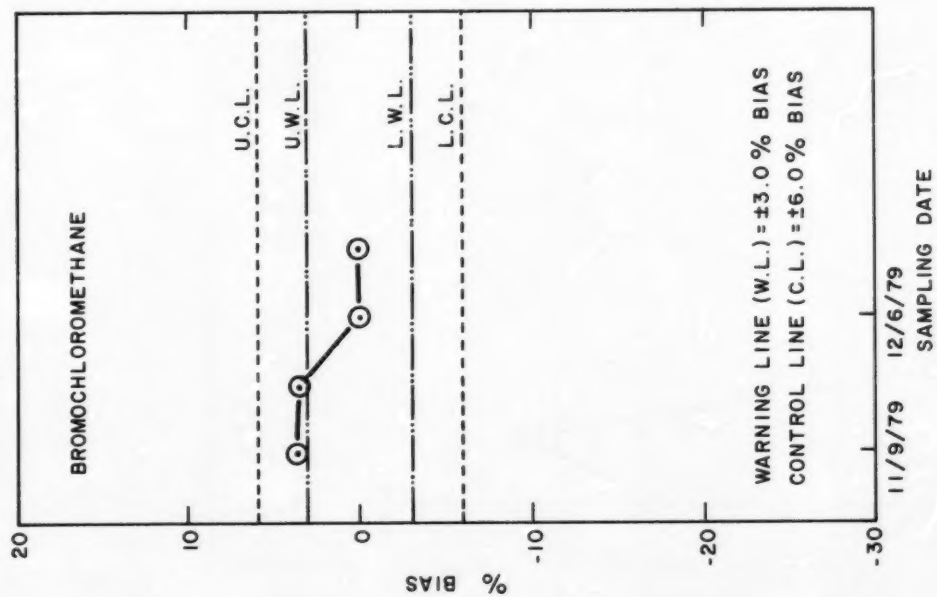


Figure C-3. Precision chart (bromochloromethane and 1-chloro-2-bromopropane) for volatile halogenated organics

TABLE C-1. ANALYSIS OF EPA REFERENCE STANDARD WS 1276*
(Volatile Halogenated Organics)

Parameter	Date	EPA True Value, µg/l	Measured Value, µg/l	% Recovery	% Bias
Chloroform	6/7	9.1	10	110	+10
	11/9	68	75	110	+10
		9.1	9.0	99	-1
Chlorodibromo- methane	6/7	68	54	79	-21
		2.7	2.6	96	-4
		17.2	19	110	+10
	11/9	2.7	2.0	111	+11
		17.2	18	105	+5
Dichlorobromo- methane	6/7	1.2	1.6	13	+33
	11/9	11.9	20	166	+66
		1.2	2.3	193	+93
		11.9	16	134	+34
Bromoform	6/7	2.8	2.8	100	0
	11/9	14.2	16	113	+13
		2.8	3.0	107	+7
		14.2	17	120	+20

*TVA Laboratory Branch data.

TABLE C-2. QUALITY ASSURANCE DATA FOR PRECURSORS

	Spiked	Found						Mean ^a	Recovery ^b	s	RSD
		375.6	359.6	391.6	359.6	367.6	359.6				
Bromide	399.6 µg Br/l	375.6	359.6	391.6	359.6	367.6	359.6	368.9	-8%	11.69	3.2%
Ammonia	85.0 µg NH ₃ /l	85.0	83.3	85.0	86.7	85.0	86.7	85.3	0.4%	1.17	1.4%
Natural Color	10.0 mg/Pt/l	10.3	10.4	10.4	10.4	10.4	10.4	10.4	4%	0.035	0.3%
Polyhydroxy-	25.0 mg Pt/l	24.7	24.8	24.9	24.9	25.0	24.8	24.8	-0.8%	0.090	0.4%
benzenes	1.0 mg/l	0.8	1.2	0.6	0.7	0.5	1.4	0.9	-13.3%	0.325	37.5%
	6.0 mg/l	6.5	5.6	4.0	5.7	5.4	5.6	5.5	8.9%	0.743	13.6%
	20 mg/l	20.3	17.8	18.0	12.2	14.7	16.6	16.6	-17.0%	2.584	15.6%
Humic Acids	1.1 mg/l	0.8	0.8	0.4	0.9	0.7	0.4	0.7	-39.4%	0.197	29.6%
Fulvic Acids	0.6 mg/l	0.0	0.3	0.4	0.4	0.7	0.4	0.4	-38.9%	0.205	56.0%

^aCalculation of recoveries from these averages may give slightly different results than those shown due to round-off.

^bThese recovery factors have not been applied to the data.

TABLE C-3. QUALITY ASSURANCE DATA FOR AMINO ACID ANALYSES

Spiked	Aspartic Acid	Threonine	Serine	Glutamic acid	Proline	Glycine	Alanine ¹	Cystine	Valine	Methionine	Isoleucine	Leucine	Tyrosine	Phenylalanine	Histidine	Lysine	Arginine	Tryptophan	Asparagine	Glutamine
PART A. EVALUATION OF ACCURACY Concentration found, µg/l																				
Spike Concentration																				
0.5 µg/l	0.6	<0.5	0.7	0.6	0.5	0.7	1.1	<0.5	<0.5	<2.0 ²	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	<0.5 ²	0.5	0.9
0.5 µg/l	0.8	0.6	1.1	0.7	0.5	0.8	0.9	0.2	0.6	<2.0 ²	<0.5	<0.5	0.5	<0.5	<0.5	0.7	<0.5	<0.5 ²	-	-
1.0 µg/l	1.2	1.1	2.0	1.4	1.3	1.4	1.4	1.3	1.1	0.3	0.9	1.2	1.4	1.6	0.9	1.2	0.7	0.5	0.2	0.9
2.0 µg/l	2.5	1.9	2.4	2.1	2.4	2.4	4.1	0.8	2.0	<2.0 ²	1.7	1.9	0.9	1.9	1.4	1.9	1.5	<0.5 ²	-	-
2.0 µg/l	2.2	2.1	2.9	2.2	2.5	2.4	4.2	1.1	1.9	<2.0 ²	1.7	1.9	1.3	2.2	1.5	2.1	1.6	<0.5 ²	-	-
50 µg/l	49.6	51.6	52.0	50.6	53.6	50.6	103.2 ¹	45.6	49.0	47.6	48.8	50.2	48.8	49.0	36.4 ³	40.6 ³	41.0	28.8	-	-
100 µg/l	93.0	99.6	103.0	97.0	100.6	96.2	196.6 ²	90.4	96.4	102.2	93.2	96.6	94.6	94.4	72.2	80.2	82.2	80.2 ³	-	-
PART B. PRECISION AND ACCURACY AT 1 nm/l LEVEL Concentration Found, µg/l ⁴																				
1.0 nm/l	1.2	1.1	1.1	1.4	1.6	0.9	0.9	1.0	1.0	1.0	1.2	1.2	1.8	1.6	1.5	1.6	1.4	2.2	-	-
1.0 nm/l	1.2	1.1	1.2	1.5	1.5	0.9	0.9	1.0	1.2	1.3	1.1	1.2	1.6	1.6	1.4	1.6	1.5	2.1	-	-
1.0 nm/l	1.2	1.1	1.0	1.4	1.6	0.9	0.9	1.0	1.1	1.2	1.1	1.2	1.7	1.6	1.5	1.6	1.5	2.1	-	-
Recovery, %	-7	-9	+6	0	+28	+19	+1	-18	-7	-2 ²	-13	-6	-8	-3	-2	+9	-12	+4	-	-
RSD, %	0.7	1.8	1.3	1.7	2.2	0.3	1.8	1.6	8.5	10.5	0.4	1.9	5.9	1.2	3.1	0.1	7.0	2.0	-	-

¹Alanine was spiked at twice the level of the other amino acids in this sample.²This compound degraded under storage at 4°C in the standard mixture used to prepare these spiked samples.³Drifting baseline may have caused these values to be low.⁴Note that measured concentrations are reported in terms of micrograms per liter for the particular compound while spikes were 1 nm/l for all compounds.

TABLE C-4. ACCURACY CHART FOR SEMIVOLATILES (BASE-NEUTRALS)

Parameters Hexachlorobenzene Date Started 6-16-79 Date Terminated 8-2-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)	
1	6-16-79	<1.0	10	17.2	17.2	172	72	
2	6-16-79	<1.0	10	9.4	9.4	93	-7	
3	6-20-79	<1.0	10	12.	12.	120	20	1 s.d. = 49%
4	6-20-79	<1.0	10	24.	24.	240	140	2 s.d. = 98%
5	6-20-79	<1.0	10	9.6	9.6	96	-4	
6	6-20-79	<1.0	10	14.6	14.6	146	46	
7	7-10-79	<1.0	10	2.2	2.2	22	-78	
8	7-10-79	<1.0	10	3.2	3.2	32	-68	
9	7-11-79	<1.0	10	4.0	4.0	40	-60	
10	7-11-79	<1.0	10	5.4	5.4	54	-46	
11	7-12-79	<1.0	10	4.6	4.6	46	-54	
12	7-12-79	<1.0	10	4.8	4.8	48	-52	
13	7-13-79	<1.0	10	8.4	8.4	84	-16	
14	7-13-79	<1.0	10	8.0	8.0	80	-20	
15	7-24-79	<1.0	60	28.	28.	47	-53	
16	7-24-79	<1.0	60	47.	47.	78	-22	
17	7-24-79	<1.0	60	46.	46.	77	-23	
18	7-24-79	<1.0	60	42.	42.	70	-30	
19	8-2-79	<1.0	60	52.	52.	87	-13	
20	8-2-79	<1.0	60	46.	46.	77	-23	

TABLE C-4. ACCURACY CHART FOR SEMIVOLATILES (BASE-NEUTRALS)
(Continued)

Parameters Hexachlorobenzene Date Started 8-7-79 Date Terminated 11-6-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	8-7-79	<1.0	60	19.	19.	32	-68
2	8-7-79	<1.0	60	16.4	16.4	27	-73
3	8-28-79	<1.0	60	48.	48.	80	-20
4	8-28-79	<1.0	60	46.	46.	77	-23
5	9-18-79	<1.0	60	46.	46.	77	-23
6	9-18-79	<1.0	60	47.2	47.2	79	-21
7	9-18-79	<1.0	60	48.	48.	80	-20
8	9-18-79	<1.0	60	46.	46.	77	-23
9	9-19-79	<1.0	60	54.6	54.6	91	-9
10	9-19-79	<1.0	60	48.	48.	80	-20
11	9-21-79	<1.0	60	54.	54.	90	-10
12	9-21-79	<1.0	60	54.	54.	90	-10
13	10-30-79	<1.0	60	45.8	45.8	76	-24
14	10-30-79	<1.0	60	47.4	47.4	79	-21
15	11-1-79	<1.0	60	48.2.	48.2	80	-20
16	11-1-79	<1.0	60	48.4	48.4	81	-19
17	11-1-79	<1.0	60	47.6	47.6	79	-21
18	11-1-79	<1.0	60	50.	50.	83	-17
19	11-6-79	<1.0	60	54.	54.	90	-10
20	11-6-79	<1.0	60	54.	54.	90	-10

TABLE C-4. ACCURACY CHART FOR SEMIVOLATILES (BASE-NEUTRALS)
(Continued)

Parameters Hexachlorobenzene Date Started 11-6-79 Date Terminated 1-17-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	11-6-79	<1.0	60	52.	52.	87	-13
2	11-6-79	<1.0	60	50.8	50.8	85	-15
3	12-18-79	<1.0	60	42.	42.	70	-30
4	12-18-79	<1.0	60	50.	50.	83	-17
5	12-18-79	<1.0	60	41.	41.	68	-32
6	12-18-79	<1.0	60	45.6	45.6	76	-24
7	12-18-79	<1.0	60	34.2	34.2	57	-43
8	12-18-79	<1.0	60	47.6	47.6	79	-21
9	1-14-80	<1.0	60	40.2	40.2	67	-33
10	1-14-80	<1.0	60	53.6	53.6	89	-11
11	1-17-80	<1.0	60	47.2	47.2	79	-21
12	1-17-80	<1.0	60	48.4	48.4	81	-19
13							
14							
15							
16							
17							
18							
19							
20							

TABLE C-5. ACCURACY CHART FOR SEMIVOLATILES (ACID EXTRACTABLES)

Parameters 2,4-Dichlorophenol Date Started 6-19-79 Date Terminated 8-2-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)	
1	6-19-79	<10	10	9.4	9.4	94	-6	
2	6-19-79	<10	10	12.	12.	120	20	
3	6-20-79	<10	10	3.2	3.2	32	-68	
4	6-20-79	<10	10	3.2	3.2	32	-68	1 s.d. = 28%
5	6-20-79	<10	10	5.4	5.4	54	-46	2 s.d. = 56%
6	6-20-79	<10	10	4.8	4.8	48	-52	
7	7-10-79	<10	10	1.6	1.6	16	-84	
8	7-10-79	<10	10	1.6	1.6	16	-84	
9	7-11-79	<10	10	0.4	0.4	4	-96	
10	7-11-79	<10	10	0	0	0	-100	
11	7-12-79	<10	10	0.8	0.8	8	-92	
12	7-12-79	<10	10	0.8	0.8	8	-92	
13	7-13-79	<10	10	4.0	4.0	40	-60	
14	7-13-79	<10	10	8.6	8.6	86	-14	
15	7-24-79	<10	60	34.	34.	57	-43	
16	7-24-79	<10	60	36.	36.	60	-40	
17	7-24-79	<10	60	36.	36.	60	-40	
18	7-24-79	<10	60	34.	34.	57	-43	
19	8-2-79	<10	60	26.	26.	43	-57	
20	8-2-79	<10	60	26.	26.	43	-57	

TABLE C-5. ACCURACY CHART FOR SEMIVOLATILES (ACID EXTRACTABLES)
(Continued)

Parameters 2,4-Dichlorophenol Date Started 8-7-79 Date Terminated 11-6-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	8-7-79	<10	60	24.	24.	40	-60
2	8-7-79	<10	60	28.	28.	47	-53
3	8-28-79	<10	60	34.	34.	56	-44
4	8-28-79	<10	60	40.	40.	67	-33
5	9-18-79	<10	60	28.	28.	47	-53
6	9-18-79	<10	60	38.	38.	64	-36
7	9-18-79	<10	60	45.	45.	75	-25
8	9-18-79	<10	60	41.	41.	68	-32
9	9-19-79	<10	60	42.6	42.6	71	-29
10	9-19-79	<10	60	54.8	54.8	91	-9
11	9-21-79	<10	60	44.	44.	72	-28
12	9-21-79	<10	60	37.6	37.6	63	-37
13	10-30-79	<10	60	42.4	42.4	71	-29
14	10-30-79	<10	60	53.2	53.2	88	-12
15	11-1-79	<10	60	32.4	32.4	54	-46
16	11-1-79	<10	60	28.2	28.2	47	-53
17	11-1-79	<10	60	31.	31.	52	-48
18	11-1-79	<10	60	34.4	34.4	57	-43
19	11-6-79	<10	60	45.	45.	75	-25
20	11-6-79	<10	60	34.6	34.6	58	-42

TABLE C-5. ACCURACY CHART FOR SEMIVOLATILES (ACID EXTRACTABLES)
(Continued)

Parameters 2,4-Dichlorophenol Date Started 11-6-79 Date Terminated 1-17-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	11-6-79	<10	60	31.6	31.6	53	-47
2	11-6-79	<10	60	24.	24.	41	-59
3	12-12-79	<10	60	30.6	30.6	51	-49
4	12-12-79	<10	60	51.8	51.8	86	-14
5	12-12-79	<10	60	43.6	43.6	73	-27
6	12-12-79	<10	60	40.8	40.8	68	-32
7	12-12-79	<10	60	39.8	39.8	66	-34
8	12-12-79	<10	60	39.4	39.4	66	-34
9	1-17-80	<10	60	37.6	37.6	63	-37
10	1-17-80	<10	60	34.8	34.8	58	-42
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

TABLE C-6. ACCURACY CHART FOR VOLATILE HOLOGENATED ORGANICS

CH ₂ ClBr							
Parameters	Bromochloromethane	Date Started	11-9-79	Date Terminated	11-9-79		
Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	11-9-79	<0.05	2.5	2.47	2.47	99	-1
2	11-9-79	<0.05	2.5	2.72	2.72	109	+9
3	11-9-79	<0.05	2.5	2.50	2.50	100	0
4	11-9-79	<0.05	2.5	2.57	2.57	103	+3
5	11-9-79	<0.05	2.5	2.50	2.50	100	0
6	11-9-79	<0.05	2.5	2.47	2.47	99	-1
7	11-9-79	<0.05	2.5	2.57	2.57	103	+3
8	11-9-79	<0.05	2.5	2.38	2.38	95	+5
9	11-9-79	<0.05	2.5	2.30	2.30	92	-8
10	11-9-79	<0.05	2.5	2.16	2.16	86	-14
11	11-9-79	<0.05	2.5	2.35	2.35	94	-6
12	11-9-79	<0.05	2.5	2.26	2.26	90	-10
13	11-9-79	<0.05	2.5	2.28	2.28	91	-9
14	11-9-79	<0.05	2.5	2.85	2.85	114	+14
15	11-9-79	<0.05	2.5	2.90	2.90	116	+16
16	11-9-79	<0.05	2.5	2.65	2.65	106	+6
17	11-9-79	<0.05	2.5	2.58	2.58	103	+3
18	11-9-79	<0.05	2.5	2.46	2.46	98	-2
19	11-9-79	<0.05	2.5	2.57	2.57	103	+3
20	11-9-79	<0.05	2.5	2.44	2.44	98	-2

1 s.d. = 4.9%

2 s.d. = 9.8%

TABLE C-6. ACCURACY CHART FOR VOLATILE HOLOGENATED ORGANICS
(Continued)

CH ₂ ClBr							
Parameters <u>Bromochloromethane</u> Date Started <u>11-9-79</u> Date Terminated <u>12-10-79</u>							
Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	11-9-79	<0.05	2.5	2.4	2.4	96	-4
2	11-9-79	<0.05	2.5	2.2	2.2	88	-12
3	11-28-79	<0.05	2.5	2.8	2.8	112	+12
4	11-28-79	<0.05	2.5	2.8	2.8	112	+12
5	12-6-79	<0.05	2.5	2.3	2.3	92	-8
6	12-6-79	<0.05	2.5	2.3	2.3	92	-8
7	12-10-79	<0.05	2.5	2.1	2.1	84	-16
8	12-10-79	<0.05	2.5	2.3	2.3	92	-8
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

TABLE C-7. ACCURACY CHART FOR VOLATILE HALOGENATED ORGANICS

$\text{CH}_2\text{ClCHBrCH}_3$
 Parameters 1-Chloro-2-Bromopropane Date Started 11-9-79 Date Terminated 11-9-79

Sample Number M	Date	$\mu\text{g/l}$ Bkg.	$\mu\text{g/l}$ Added	$\mu\text{g/l}$ Obs.	$\mu\text{g/l}$ Rec.	% Rec.	% Bias (% Rec. -100)	
1	11-9-79	<0.05	2.5	2.4	2.4	96	-4	
2	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
3	11-9-79	<0.05	2.5	2.5	2.5	100	0	
4	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
5	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
6	11-9-79	<0.05	2.5	2.5	2.5	100	0	
7	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
8	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
9	11-9-79	<0.05	2.5	2.2	2.2	88	-12	
10	11-9-79	<0.05	2.5	2.3	2.3	92	-8	
11	11-9-79	<0.05	2.5	2.5	2.5	100	0	
12	11-9-79	<0.05	2.5	2.3	2.3	92	-8	1 s.d. = 3.6%
13	11-9-79	<0.05	2.5	2.5	2.5	100	0	2 s.d. = 7.1%
14	11-9-79	<0.05	2.5	2.7	2.7	108	8	
15	11-9-79	<0.05	2.5	2.7	2.7	108	8	
16	11-9-79	<0.05	2.5	2.6	2.6	104	+4	
17	11-9-79	<0.05	2.5	2.5	2.5	100	0	
18	11-9-79	<0.05	2.5	2.5	2.5	100	0	
19	11-9-79	<0.05	2.5	2.4	2.4	96	-4	
20	11-9-79	<0.05	2.5	2.5	2.5	100	0	

TABLE C-7. ACCURACY CHART FOR VOLATILE HALOGENATED ORGANICS
(Continued)



Parameters 1-Chloro-2-Bromopropane Date Started 11-19-79 Date Terminated 12-10-79

Sample Number M	Date	µg/l Bkg.	µg/l Added	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)
1	11-19-79	<0.05	2.5	2.4	2.4	96	-4
2	11-19-79	<0.05	2.5	2.3	2.3	92	-8
3	11-28-79	<0.05	2.5	2.4	2.4	96	-4
4	11-28-79	<0.05	2.5	2.5	2.5	100	0
5	12-6-79	<0.05	2.5	2.3	2.3	92	-8
6	12-6-79	<0.05	2.5	2.3	2.3	92	-8
7	12-10-79	<0.05	2.5	2.5	2.5	100	0
8	12-10-79	<0.05	2.5	2.5	2.5	100	0
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

TABLE C-8. RESULTS OF EPA REFERENCE SAMPLES - WS 1276
(Volatile Halogenated Organics)

Chloroform, Bromoform,
Dichlorobromomethane,
Parameters Chlorodibromomethane Date Started 6-7-79 Date Terminated 6-7-79

Sample Number M	Date	Sample I.D.	µg/l EPA True Value	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)	Parameter
1	6-7-79	#1	9.1	10.	10.	110	10	CHCl ₃
2	6-7-79	#2	68.	75.	75.	110	10	CHCl ₃
3								
4	6-7-79	#1	12.	20.	20.	166	66	CHCl ₂ Br
5	6-7-79	#2	1.2	1.6	1.6	133	33	CHCl ₂ Br
6								
7	6-7-79	#1	2.7	2.6	2.6	96	-4	CHClBr ₂
8	6-7-79	#2	17.2	19.	19.	110	10	CHClBr ₂
9								
10	6-7-79	#1	2.8	2.8	2.8	100	0	CHBr ₃
11	6-7-79	#2	14.2	16.	16.	113	13	CHBr ₃
12								
13								
14								
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TABLE C-8. RESULTS OF EPA REFERENCE SAMPLES - WS 1276
(Volatile Halogenated Organics)
(Continued)

Chloroform, Bromoform,
Dichlorobromomethane,
Parameters Chlorodibromomethane Date Started 11-9-79 Date Terminated 11-9-79

Sample Number M	Date	Sample I.D.	µg/l EPA True Value	µg/l Obs.	µg/l Rec.	% Rec.	% Bias (% Rec. -100)	Parameter
1	11-9-79	#1	9.1	9.0	9.0	99	-1	CHCl ₃
2	11-9-79	#2	68.	54.	54.	79	-21	CHCl ₃
3								
4	11-9-79	#1	1.19	2.3	2.3	193	+93	CHCl ₂ Br
5	11-9-79	#2	11.9	16.	16.	134	+34	CHCl ₂ Br
6								
7	11-9-79	#1	2.7	3.0	3.0	111	+11	CHClBr ₂
8	11-9-79	#2	17.2	18.	18.	105	+5	CHClBr ₂
9								
10	11-9-79	#1	2.8	3.0	3.0	107	+7	CHBr ₃
11	11-9-79	#2	14.2	17.	17.	120	+20	CHBr ₃
12								
13								
14								
15								
16								
17								
18								
19								
20								

TABLE C-9. PRECISION CHART FOR SEMIVOLATILES (Base-Neutrals)

Parameters		Hexachlorobenzene		Date Started		6-16-79		Date Terminated		11-6-79	
Sample Number M	Date	µg/l No. 1	µg/l No. 2	Diff. (di)	Mean	S.D. (di x 0.89)	%RSD	1 s.d. =	2 s.d. =	42%	
					($\frac{\text{No.1}+\text{No.2}}{2}$)		($\frac{\text{SD}}{\text{mean}}$ x 100)				
1	6-16-79	17.2	9.4	7.8	13.3	6.9	52.2				
2	6-20-79	12.	24.	12.	18.	10.7	59.3				
3	6-20-79	9.6	14.6	5.0	12.1	4.4	36.8	1 s.d. =			
4	7-10-79	2.2	3.2	1.0	2.7	.89	33.0		21%		
5	7-11-79	4.0	5.4	1.4	4.7	1.2	26.5	2 s.d. =			
6	7-12-79	4.6	4.8	0.2	4.7	.178	3.8		42%		
7	7-13-79	8.4	8.0	0.4	8.2	.356	4.3				
8	7-24-79	28.	47.	19.	37.5	16.9	45.1				
9	7-24-79	46.	42.	4.	44.	3.56	8.1				
10	8-2-79	52.	46.	6.0	49.	5.3	10.9				
11	8-7-79	19.	16.4	2.6	17.7	2.3	13.1				
12	8-28-79	48.	46.	2.0	47.	1.78	3.8				
13	9-18-79	47.4	47.2	0.2	47.3	.178	0.4				
14	9-18-79	48.	46.	2.0	47.	1.78	3.8				
15	9-19-79	54.6	48.	6.6	51.3	5.9	11.5				
16	9-21-79	54.	54.	0	27.	0	0				
17	11-1-79	48.2	48.4	0.2	48.3	.178	.37				
18	11-1-79	47.6	50.	2.4	48.8	2.14	4.4				
19	11-6-79	54.	54.	0	54.	0	0				
20	11-6-79	52.	50.8	1.2	51.4	1.07	2.1				

TABLE C-9. PRECISION CHART FOR SEMIVOLATILES (Base-Neutrals)
(Continued)

Parameters		Hexachlorobenzene		Date Started		Date Terminated	
				12-18-79		1-17-80	
Sample Number	Date	µg/l No. 1	µg/l No. 2	Diff. (di)	Mean $(\frac{\text{No.1}+\text{No.2}}{2})$	S.D. (di x 0.89)	%RSD $(\frac{\text{SD}}{\text{mean}} \times 100)$
M							
1	12-18-79	42.	50.	8.	46.	7.12	15.5
2	12-18-79	41.	45.6	4.6	43.3	4.1	9.4
3	12-18-79	34.2	47.6	13.4	40.9	11.9	29.2
4	1-14-80	40.2	53.6	13.4	46.9	11.9	25.4
5	1-17-80	47.2	48.4	1.2	47.8	1.07	2.2
6							
7							
8							
9							
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TABLE C-10. PRECISION CHART FOR VOLATILE HALOGENATED ORGANICS

Parameters		1,4-Dichlorobutane		Date Started		6-6-79		Date Terminated		9-15-79	
Sample Number											
M	Date	µg/l No. 1	µg/l No. 2	Diff. (di)	Mean ($\frac{\text{No. 1} + \text{No. 2}}{2}$)	S.D. (di x 0.89)	%RSD ($\frac{\text{SD}}{\text{mean}}$ x 100)				
1	6-6-79	2.26	2.30	0.04	2.28	0.036	1.6				
2	6-13-79	2.28	2.40	0.12	2.34	0.107	4.6				
3	6-14-79	2.57	2.54	0.03	2.56	0.027	1.0	1 s.d. =			
4	6-21-79	2.40	2.38	0.02	2.39	0.018	0.7	1.7%			
5	6-28-79	2.25	2.26	0.01	2.26	0.009	0.4	2 s.d. =			
6	6-28-79	2.29	2.19	0.10	2.24	0.089	4.0	3.4%			
7	6-29-79	2.26	2.34	0.08	2.30	0.071	3.1	~ 2%			
8	7-16-79	2.58	2.46	0.12	2.52	0.107	4.2	~ 4%			
9	7-16-79	2.68	2.67	0.01	2.68	0.009	0.3				
10	7-30-79	2.58	2.67	0.09	2.62	0.080	3.0				
11	7-30-79	2.43	2.38	0.05	2.40	0.044	1.8				
12	8-8-79	2.22	2.22	0	2.22	0	0				
13	8-14-79	2.18	2.16	0.02	2.17	0.018	0.8				
14	8-23-79	1.92	1.98	0.06	1.95	0.050	2.7				
15	9-13-79	1.98	2.10	0.12	2.04	0.107	5.2				
16	9-14-79	2.00	2.00	0	2.00	0	0				
17	9-15-79	1.76	1.76	0	1.76	0	0				
18											
19											
20											

TABLE C-11. PRECISION CHART FOR SEMIVOLATILES (Acid Extractables)

Parameters 2,4-Dichlorophenol Date Started 6-19-79 Date Terminated 11-6-79

Sample Number M	Date	$\mu\text{g/l}$ No. 1	$\mu\text{g/l}$ No. 2	Diff. (di)	Mean $(\frac{\text{No.1}+\text{No.2}}{2})$	S.D. (di x 0.89)	%RSD $(\frac{\text{SD}}{\text{mean}} \times 100)$	
1	6-19-79	9.4	12.0	2.6	10.7	2.31	21.6	
2	6-20-79	3.2	3.2	0	3.2	0	0	
3	6-20-79	5.4	4.8	0.6	5.1	0.53	10.5	1 s.d. =
4	7-10-79	1.6	1.6	0	1.6	0	0	65%
5	7-11-79	0.4	0.0	0.4	0.2	.40	178.	2 s.d. =
6	7-12-79	0.8	0.8	0	0.8	0	0	130%
7	7-13-79	4.0	8.6	4.6	6.4	4.1	64.	
8	7-24-79	34.	36.	2.0	35.	1.78	5.1	
9	7-24-79	36.	34.	2.0	35.	1.78	5.1	
10	8-2-79	26.	26.	0	26.	0	0	
11	8-7-79	24.	28.	4.0	26.	3.56	13.7	
12	8-28-79	34.	40.	6.0	37.	5.34	14.4	
13	9-18-79	28.	38.	10.	33.	8.9	27.0	
14	9-18-79	45.	41.	4.0	43.	3.56	10.8	
15	9-19-79	42.6	54.8	12.2	48.7	10.8	22.3	
16	9-21-79	44.	37.6	6.4	40.8	5.7	14.	
17	10-30-79	42.4	53.2	10.8	47.8	9.6	20.1	
18	11-1-79	32.4	28.2	4.2	30.3	3.73	12.3	
19	11-1-79	31.	34.4	3.4	32.7	3.0	9.2	
20	11-6-79	45.	34.6	10.4	39.8	9.3	23.4	

TABLE C-11. PRECISION CHART FOR SEMIVOLATILES (Acid Extractables)
(Continued)

Parameters 2,4-Dichlorophenol Date Started 11-6-79 Date Terminated 1-17-80

Sample Number M	Date	$\mu\text{g/l}$ No. 1	$\mu\text{g/l}$ No. 2	Diff. (di)	Mean $(\frac{\text{No. 1} + \text{No. 2}}{2})$	S.D. (di x 0.89)	%RSD $(\frac{\text{SD}}{\text{mean}} \times 100)$
1	11-6-79	31.6	24.	7.6	27.8	6.76	24.3
2	12-12-79	30.6	51.8	21.2	41.2	18.9	46.
3	12-12-79	40.8	43.6	2.8	42.2	2.49	5.9
4	12-12-79	39.8	39.4	0.4	39.6	.356	2.5
5	1-17-80	37.6	34.8	2.8	36.2	2.49	6.9
6	1-17-80	35.8	40.6	4.8	38.2	4.27	11.2
7							
8							
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TABLE C-12. PRECISION CHART FOR VOLATILE HALOGENATED ORGANICS

Parameters Bromochloromethane (CH₂ClBr) Date Started 11-9-79 Date Terminated 11-9-79

Sample Number M	Date	µg/l No. 1	µg/l No. 2	Diff. (di)	Mean ($\frac{\text{No. 1} + \text{No. 2}}{2}$)	S.D. ($\text{di} \times 0.89$)	%RSD ($\frac{\text{SD}}{\text{mean}} \times 100$)
1	11-9-79	2.47	2.72	0.25	2.60	0.22	8.5
2	11-9-79	2.50	2.57	0.07	2.54	0.06	2.4
3	11-9-79	2.50	2.47	0.03	2.49	0.03	1.2
4	11-9-79	2.57	2.38	0.19	2.48	0.17	6.9
5	11-9-79	2.30	2.16	0.14	2.23	0.12	5.4 1 s.d. =
6	11-9-79	2.35	2.26	0.09	2.30	0.08	3.5 $\approx$ 5%
7	11-9-79	2.28	2.85	0.57	2.56	0.51	19.9 2 s.d. =
8	11-9-79	2.90	2.65	0.25	2.78	0.22	7.9 $\approx$ 10%
9	11-9-79	2.58	2.46	0.12	2.52	0.11	4.4
10	11-9-79	2.57	2.44	0.13	2.50	0.12	4.8
11	11-19-79	2.4	2.2	0.2	2.3	0.18	7.7
12	11-28-79	2.8	2.8	0	2.8	0	0
13	12-6-79	2.3	2.3	0	2.3	0	0
14	12-10-79	2.4	2.3	0.1	2.4	0.09	3.8
15							
16							
17							
18							
19							
20							

TABLE C-13. PRECISION CHART FOR VOLATILE HALOGENATED ORGANICS

Parameters $\text{CH}_2\text{ClCHBrCH}_3$ 1-Chloro- 2-Bromopropane Date Started 11-9-79 Date Terminated 12-10-79

Sample Number M	Date	$\mu\text{g/l}$ No. 1	$\mu\text{g/l}$ No. 2	Diff. (di)	Mean $(\frac{\text{No.1}+\text{No.2}}{2})$	S.D. (di x 0.89)	%RSD $(\frac{\text{SD}}{\text{mean}} \times 100)$
1	11-9-79	2.4	2.6	0.2	2.5	0.18	7.2
2	11-9-79	2.5	2.6	0.1	2.6	0.09	0.3
3	11-9-79	2.6	2.5	0.1	2.6	0.09	0.3
4	11-9-79	2.6	2.6	0	2.6	0	0
5	11-9-79	2.2	2.3	0.1	2.2	0.09	4.0 1 s.d. =
6	11-9-79	2.5	2.3	0.2	2.4	0.12	7.4 $\approx 3.0\%$
7	11-9-79	2.5	2.7	0.2	2.6	0.18	6.9 2 s.d. =
8	11-9-79	2.7	2.6	0.1	2.6	0.09	3.4 $\approx 6\%$
9	11-9-79	2.5	2.5	0	2.5	0	0
10	11-9-79	2.4	.25	0.1	2.4	0.09	3.6
11	11-19-79	2.4	2.3	0.1	2.4	0.09	3.8
12	11-28-79	2.4	2.5	0.1	2.4	0.09	3.6
13	12-6-79	2.3	2.3	0	2.3	0	0
14	12-10-79	2.5	2.5	0	2.5	0	0
15							
16							
17							
18							
19							
20							

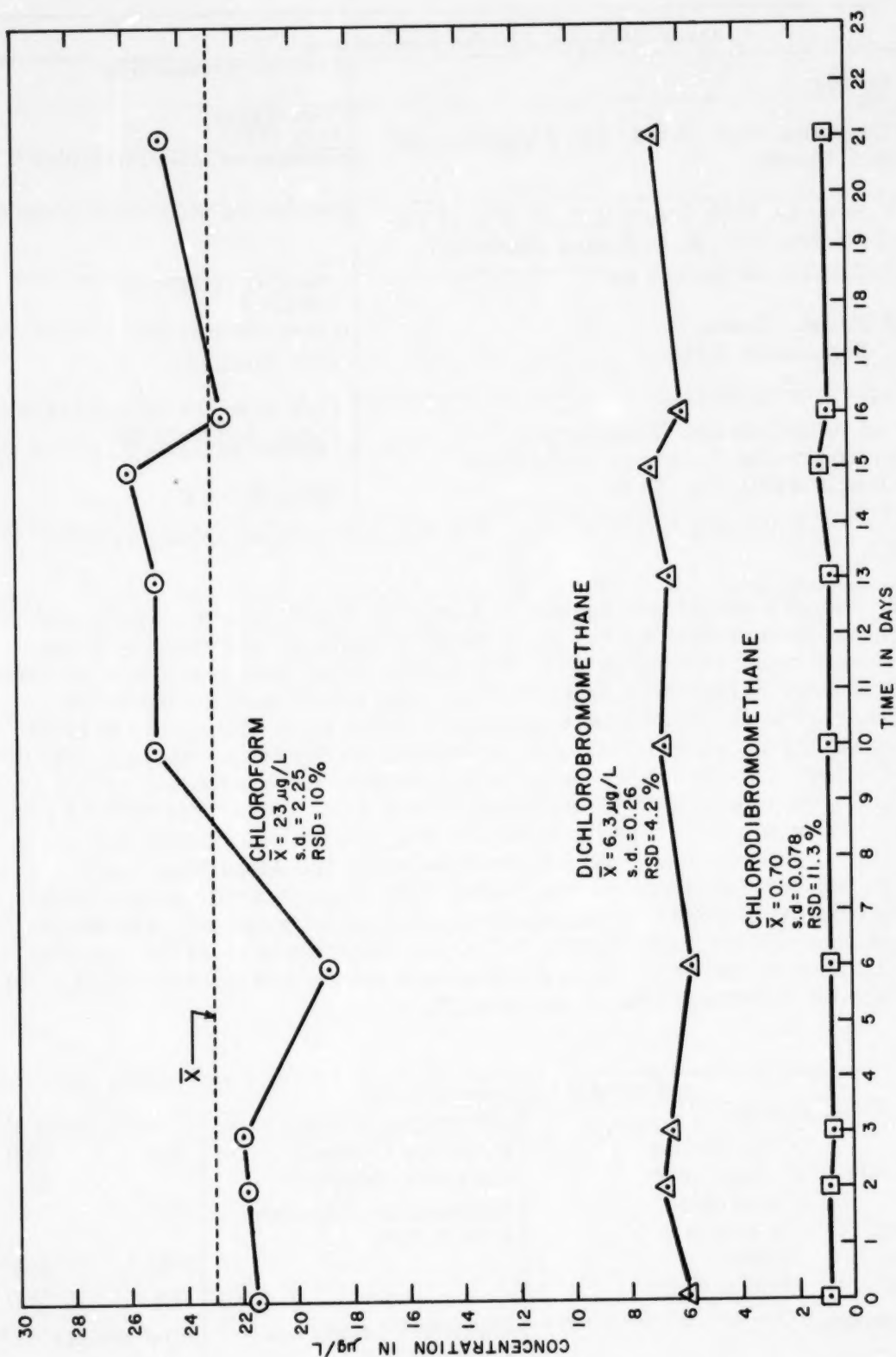


Figure C-4. Chloroform, dichlorobromomethane, dibromochloromethane
 Concentration of volatile organics versus time stored
 (Each sample was quenched with sodium thiosulfate)